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INFRA-RED EMISSION SPECTRA.[1]

By William W. Coblentz.

THE present experimental investigation was performed in the Physical Laboratory of Cornell University during the academic year 1904–1905. It forms the second part of an investigation of infra-red radiation, rendered possible by a grant from the Carnegie Institution of Washington. The first grant was for "Investigating infra-red emission and absorption spectra." Finding it impossible to complete the work in the time allotted, the Institution very generously renewed the grant, and the writer takes this opportunity to express his gratitude for the assistance rendered. In the Physical Laboratory he is under deep obligations to Professors E. L. Nichols and E. Merritt for advice and criticisms as well as for the numerous facilities placed at his disposal. His dealings with the two institutions have been so agreeable that it is with a feeling of regret that additional phases of the work could not be continued with them.

The present investigation deals with the question of the distribution of emission lines (bands) in the infra-red, especially with the question of presence of lines beyond $1.5\,\mu$. All the infra-red lines predicted by our spectral series formulæ end in the short wavelength just beyond the red. Any information as to the presence of lines beyond this point will aid in establishing these formulæ upon

[1] Extracts from a memoir on this subject submitted to the Carnegie Institution of Washington for publication.

a firmer, less empirical basis than they have at present. From our knowledge of the radiation from the "black body," which is most intense in the region of 1.2 μ to 2.5 μ at high temperatures, one would expect the emission bands at 2 μ, if there be any, to be just as intense as those found by Snow[1] at 1 μ. Other points of interest which developed as the work progressed will be noted in their proper places.

All observers agree in thinking that when radiation is emitted by a gas, in one case by heating it, and in another case by sending an electric current through it, the mechanism which is brought into play must differ in some important respects in the two cases. The present work deals with the radiation from a gas when a current is sent through it.

The work divides itself into two parts, viz., emission spectra of the arc between metallic electrodes and of the chlorides of the alkali metals in the carbon arc; and emission spectra of gases in vacuum tubes. The contrast between these two forms of radiators is worthy of notice. The arc is noted for its enormous heat radiation in proportion to its light radiation. On the other hand the vacuum tube radiates but little heat. Consequently, in the study of these two kinds of radiators, the form of the device for exploring their spectra must differ. If a radiometer is used the period must be short, for the arc, to avoid heating of the window and the consequent shifting of the zero reading. This, however, is of less importance than the variation in intensity of the radiation from the arc which requires a recording instrument having a short period.

For the vacuum tube a much greater sensitiveness must be used, which means a longer period for a linear radiometer vane. Fortunately the radiation from the vacuum tube is uniform, which permits the use of an instrument having a slow period.

In the present work a Nichols radiometer, a 7 cm. rock-salt prism and a 35 cm. focal length mirror spectrometer were used.[2]

For the emission spectra of the metals, the radiometer vanes had an area of about 2 × 15 mm. each, and the short period was due to

[1] Snow, PHYS. REV., 1, p. 35, 1893.

[2] Described in the PHYS. REV., 16, pp. 35 and 77, 1903, and in "Infra-red Investigations," Washington, D. C. Published by the Carnegie Institution, October, 1905.

the heavy fiber suspension. The vacuum tube radiation being very weak, required great sensitiveness, which was obtained in part by reducing the size of the vanes (of mica) to 1 × 10 mm. and selecting a fine fiber. The behavior of such a vane is entirely different from a heavier one. At low pressures the vane before the window was suddenly repelled from it, due apparently to the radiation from the window. This repulsion occurred when both vanes were black, and when the unexposed one was not covered with lamp-black. It was not due to electrification, and throughout the vacuum tube work it was necessary to use a torsion head to keep the deflection on the scale.

I. Infra-red Emission Spectra of Metals.

This work was begun by examining the spark spectra of such metals like Zn, Al and Cu. An induction coil and condenser were used. No emission lines could be detected; instead of lines a weak continuous radiation was detected in the region of 2 μ to 3 μ, which appeared to be due to the hot particles from the electrodes. The arc between metallic electrodes of Fe, Zn and Cu was then tried; but no lines could be detected in the region of 1 μ, beyond which point the incandescent oxides gave such an intense continuous, "black body," spectrum that the emission lines would have been obliterated by the radiation from the oxides. The vapors from the copper arc had but little "black body" radiation. No emission lines were detected, however, although several have been predicted in the region of 2.5 μ.

In the Zn arc the oxides are formed so rapidly that it is almost impossible to work with this metal. The problem then is to separate the black body radiation of the oxides from that of the vapors, which is very different from the work in the visible spectrum.

Chlorides of Metals.

The chlorides of Na, Li and K were then examined in the carbon arc, using for the purpose hollow carbon electrodes filled with the salt. The carbons used varied from 6 to 9 mm. in diameter, the holes being from 1.4 to 2.5 mm. A direct current of 15 amp. from a 104-volt circuit was used. The radiometer slit was reduced

to 0.1 mm. in width, nevertheless the radiation at 2 μ, which at the most gave a deflection of only a few millimeters was not resolved into individual lines. This is in marked contrast with the strong emission lines at 1 μ, and as will be noticed later on, the continuous radiation at 2 μ would blot out any weak emission lines, as far as a radiometer or a bolometer is concerned. Here a photographic process would be better since the effect upon the plate is cumulative, and one would have dark lines superposed upon a dark background, just as Abney and Festing [1] found for their absorption spectra at 1 μ.

Carbon Arc.

In Fig. 1 is given the emission spectrum of the carbon electrodes, curve *a*, and that of the violet vapor of the arc, curve *b*. It will be noticed that there is but little radiation from the vapor except a

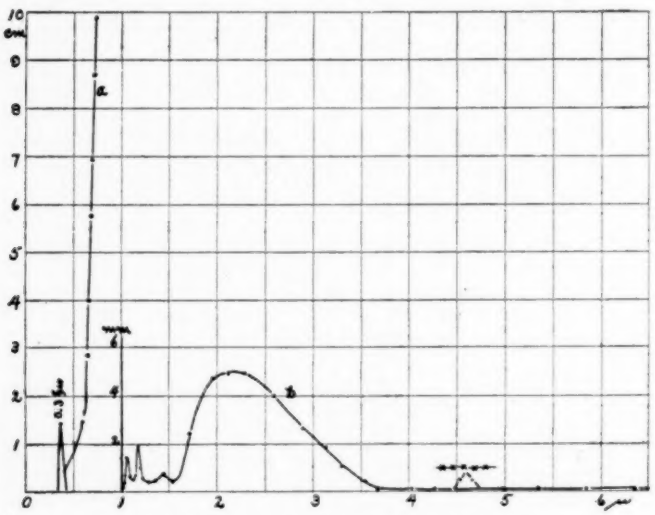

Fig. 1. Carbon arc ; *a* = electrodes, *b* = vapor.

slight amount from 2 μ to 3 μ. On the other hand the deflection was thrown off the scale for the radiation from the electrodes, just beyond the red. Snow [2] found the radiation from the arc vapors concentrated in a single line, in the violet, at 0.385 μ. This line is four times as intense as the one at 1.09 μ. In the present work

[1] Abney and Festing, Phil. Trans., 177, p. 887, 1882.
[2] Snow, PHYS. REV., 1, p. 35, 1893.

the lines are of about equal intensity, due in part to the loss of intensity of the violet line, caused by the radiometer window. A new line occurs at 1.2 μ, while on a thorough reëxamination no line was found at 4.52 μ. This is of considerable interest since it shows that no CO_2 is formed, and that the electrodes are consumed in a different manner. They do not disappear in the ordinary form of combustion. There is but little residue from mechanical disintegration; they disappear chiefly in the form of vapor. The absence of radiation from the carbon vapors is in marked contrast with the radiation from the electrodes, any trace of which, as already mentioned, was sufficient to cause large deflections. The black body radiation is not very intense at a low temperature and the maximum lies beyond 3 μ. The oxides in the arc have a high temperature; the maximum lies at 2 μ and the weak radiation in this region is to be attributed to the low density of the vapors.

Sodium, Na.

Snow (*loc. cit.*) found that the salts of the metals gave the same emission lines as the metal itself, and that the chlorides were well adapted for emission spectra work, using hollow carbon electrodes.

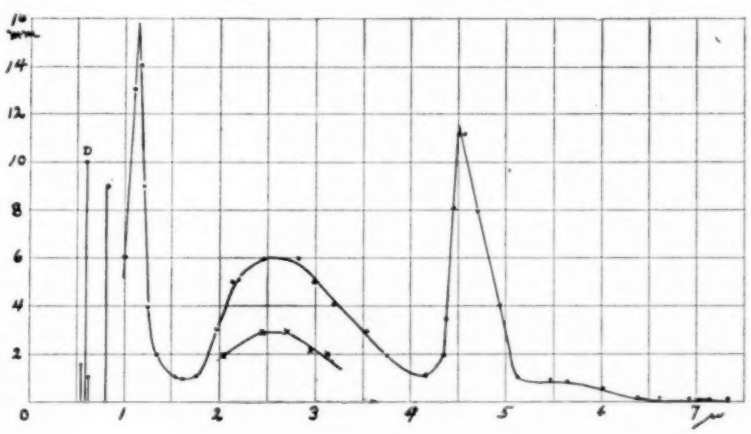

Fig. 2. Na.

For this reason only the chlorides of the metals were used. The present work was not concerned with the verification of his results, which were used only in comparing the relative intensity of the lines

investigated. He used a quartz prism, which on account of its larger dispersion permits a greater accuracy in determining wave-lengths. In the present work the question was whether there are lines beyond the region investigated by him. The distribution of the energy in the vapor of Na is shown in Fig. 2.

Snow found the intensities of the lines at 0.589 μ, 0.818 μ and 1.13 μ to have a ratio of 87 : 66 : 42. In other words the energy in 0.589 μ is more than twice that of the line at 1.132 μ. In the present work the intensities of these two lines are exactly reversed, and in the same proportion. Since the dispersion is smaller this may be due to the impurity of the spectrum.

From 2 μ to 3 μ there is a weak continuous radiation, which appears to be due to the oxides of the metals in the arc.

For Li this is not so intense, and, since the solid material (dust) coming from the arc is also less, the evidence is strengthened in favor of the emission at 2 μ to 3 μ being due to oxides. The emission band at 4.52 μ is also to be noticed. Since it occurs only

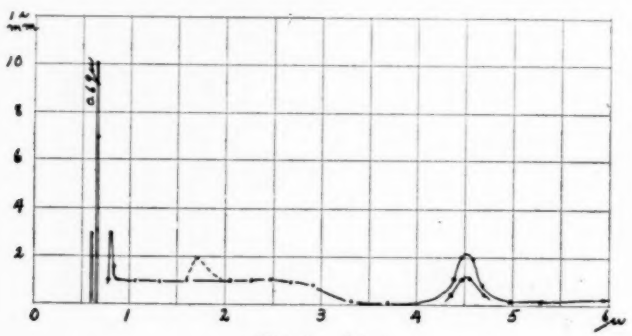

Fig. 3. Li.

when the salts of the metals are in the arc, and is *not* to be found in the carbon arc its source remains undetermined. If it be due to CO_2, from the air, then from the shifting of the maximum to the longer wave-lengths (found by Paschen, *loc. cit.*, being at 4.40 μ for the bunsen flame) it would appear that the temperature of the arc is about 4,000° absolute.

Lithium, Li.

The chloride of lithium vaporizes so easily that no true measure of the radiation from the dense vapor could be obtained. In like

manner the radiation from the oxides at 2 μ to 3 μ is also weak. The bands at 0.67 μ and 0.811 μ (Fig. 3) have the same ratio of intensity as found by Snow. Beyond this point no lines could be detected, except a slight band at 4.52 μ.

Potassium, K.

In Fig. 4 is shown the emission curve of potassium. The KCl does not vaporize so easily as LiCl and is readily adapted to the arc. Snow found strong lines at 0.768 μ, 1.155 μ and 1.22 μ, the first one being four times that of the band at 1.15 μ. In the present work the last two lines were not not quite resolved and no comparison can be made. The band at 1.47 μ was also found by Snow. The usual region of continuous radiation is found from 2 μ to 3 μ. The 4.52 μ emission band is strong. The emission band of CO_2 at

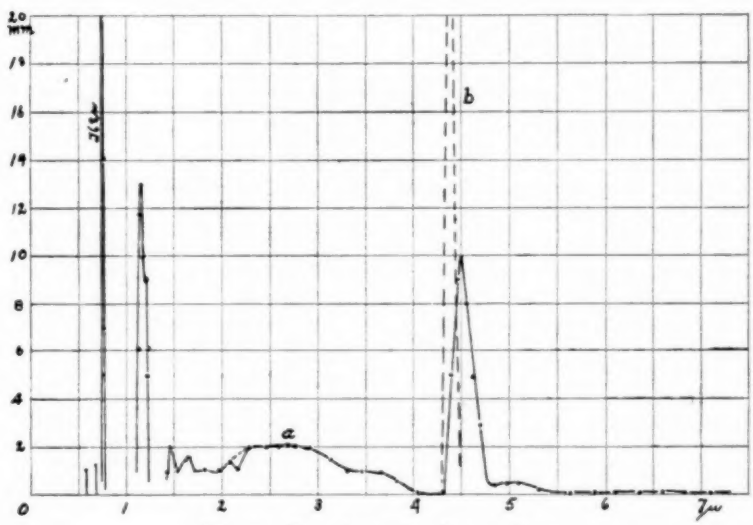

Fig. 4. Potassium ; b = Bunsen flame.

4.40 μ, using a bunsen burner, is also given, curve b, — the latter is three times (deflection equals 3.2 cm.) as strong as the band at 4.52 μ.

As a whole from these curves it will be noticed that no emission lines occur beyond 2 μ, which is entirely unexpected. Beyond this point a weak emission line would be obliterated by the continuous spectrum. The band at 4.52 μ will be noticed shifted to 4.75 μ

in the vacuum tube radiation. The intensity of the emission lines found depends upon the density of the metallic vapor in the arc. From the fact that no lines were observed beyond those found by Snow it is not to be inferred that no lines lie beyond $2\,\mu$. The work simply shows that, for the conditions which produce the lines at the end of the red, no lines of measurable intensity are to be found beyond this point. It is true that Lehmann[1] has just shown that Rb and Cs have lines at $1.7\,\mu$; but the emission curves of these two elements, found by Snow, also show *weak* lines in this region, and it is only the cumulative effect upon the phosphor-photographic plate that has enabled Lehmann to map them.

II. Infra-red Emission Spectra of Gases in Vacuum Tubes.

Since the incandescent oxides in the arc and spark emit a continuous spectrum of sufficient intensity to obliterate any weak emission lines, beyond 2μ, it is impossible to detect them. The vacuum tube lacks these defects, and is adapted to this work provided one has sensitive apparatus to detect the radiation emitted.

The dispersed infra-red radiation from gases in a vacuum tube is of considerable interest in comparison with the radiation of gases in a flame. The work of Julius[2] and of Paschen[3] shows that by mere temperature elevation gases emit characteristic discontinuous spectra. From a theoretical standpoint such an investigation is also of importance, since all the infra-red lines predicted by our spectral series formulæ end in the short wave-lengths just beyond the red. This presents the interesting question whether emission lines are to be found beyond the region of $2\,\mu$. In this connection a recent theoretical paper by Garbasso[4] is to be noticed in which he maintains that the series of Kayser and Runge have a real existence.

In the preliminary part of this work the vacuum tube used by Drew[5] was employed. In this tube the electrodes were at right angles to and at a short distance from the main part which formed the positive column. Several rubber joints were in series with the

[1] Lehmann, Phys. Zeit., 5, 823, 1904.
[2] Julius, Licht u. Wärmestrahlung verbrannter Gase, Berlin, 1890.
[3] Paschen, Ann. der Physik., 3, 53, p. 334, 1894.
[4] Garbasso, Nuovo Cimento, 9, p. 113, 1905.
[5] Drew, PHYS. REV., 17, p. 321, 1903.

mercury pump, McLeod gauge and the vacuum tube. Several gases were examined, all of which, except hydrogen, showed an emission band in common at 4.75 μ. Hoping to gain intensity of the radiation, a tube was made similar to one used by Runge and Paschen.[1] The aluminum electrodes were 2.5 cm. long, and 2.8 cm. diameter, through which the radiation passed axially into the spectrometer slit of 8 mm. length and 1 mm. width. The radiometer slit was 0.7 mm. The internal diameter of the main portion of the vacuum tube was 1 cm. and its length was from 15 to 18 cm. The window was of rock salt secured on the outside by means of bees-wax covered with shellac varnish. The window was also secured by means of shellac which had been boiled until it thickened. To avoid rubber joints the vacuum tube was sealed to the pump and the gases introduced through a barometric column of mercury. The tube was air tight but, at a low pressure, it would become so hot that vapors would be given off and the cathode luminescence would disappear. This luminescence would reappear after the tube had cooled. According to Travers (Study of Gases), this is due to gases absorbed by the electrodes. At any rate it did not interfere with the work, since the tube was used at such a pressure that it did not become heated. All evidence indicated that the impurity band at 4.75μ, which was found in all the gases in the preliminary work was due to something that entered with the gas; and it was finally shown to be due to contamination with CO_2 while making the gas. The problem then was to make a gas which was free from even slight traces of CO_2. Previous experience showed that to bubble a gas through several purifying solutions in series with the pump was not sufficient. Hence, in preparing such a gas like CO, an ordinary mercury gas pipette was used. The gas was washed back and forth from the mercury pipette, through a tube containing P_2O_5 into a pipette of KOH, for about half an hour, to free it from CO_2 and to dry it. After such a treatment nitrogen and oxygen did not show the impurity band at 4.75 μ.

The residual gas in the pump and glass connecting tubes was swept out by passing a discharge through it and heating it from the outside.

[1] Runge and Paschen, Astrophys. Jour., 3, p. 4, 1896.

A large Charpintier and also a Max Kohl No. 4 induction coil were used to excite the vacuum tube. For convenience, for most of this work, the primary was connected directly through a rheostat to a 104 volt, 60 or 120 cycle, alternating current.

An ammeter was placed in the primary circuit, while an a. c. millivoltmeter having a resistance of 21,760 ohms was used to measure the current in the secondary.

The primary current varied from 3 to 6 amp., and the secondary from 0.012 to 0.028 ampere.

Since the spectrometer arm was movable, the vacuum tube had to be adjusted before the slit, by hand. The points on the curves given are usually the mean of several readings.

Observations were made for constant current in secondary and variable pressure, and also for constant pressure and variable current.

The method of observation consisted in obtaining the radiometer deflection for the gas when the discharge was passing and then, after stopping the discharge, allowing the deflection to return towards its original zero reading. The hot cell would prevent the deflection from returning to the original zero in 50 seconds (radiometer period) and the difference in the two zero readings gave approximately the deflection due to the hot cell. Another method for finding the deflection due to the hot cell consisted in passing the discharge for 50 seconds, then on stopping the discharge and raising the shutter reading the deflection. Of course the cell cools somewhat while obtaining the deflection, but it is not a great amount in comparison with the total deflection. Since the cell became heated the least at 0.6 to 1 mm., it was used at this pressure. In the region up to 1.5 μ *no* radiation from the hot cell could be detected. Beyond 3 μ, for a pressure of 0.6 to 1 mm., the deflections often amounted to several centimeters. On the other hand nitrogen shows strong lines at 1 μ which would indicate that if nitrogen emits bands on account of its thermal condition, then it must be at a *higher temperature* than the cell.

Water Vapor, H_2O.

After finding the impurity band at 4.75 μ in all the gases except hydrogen, and knowing that water has an absorption band at this

point, a special attachment was provided to introduce water into the previously exhausted pump and vacuum tube.

The emission spectrum was found for various pressures, up to 3 mm., but no emission bands were found. On the contrary, the hot cell, after stopping the discharge, gave deflections which were as large as those for the vapor. With water vapor the cell became much hotter than for the other gases.

A slight trace of water vapor has a great effect in depressing the intensity of the emission lines as was found on allowing air to enter the tube; and only after filling the tube several times with air and exhausting it did the air lines, at 0.9 μ, 1.05 μ and 4.75 μ, appear in their usual intensity.

It will be noticed that the water vapor has *no* emission lines, which is true of the vapor in a bunsen or oxyhydrogen flame. On the the other hand alcohol vapor shows quite a strong emission spectrum from 2 μ to 3 μ. This is probably due to the difference in density of the two vapors.

Hydrogen, H.

This sample of hydrogen was generated from Zn + HCl and dried in H_2SO_4 and in P_2SO_5.

In the region of 1 μ energy is radiated which may be due to slight traces of nitrogen. *No* emission band is to be found at 4.75 μ. The radiation curve for the hot cell (observations plotted in circles) coincides with that of the gas.

Oxygen, O.

The first sample of oxygen, made by heating $KClO_3 + MnO_2$, showed the impurity band at 4.75 μ and no further examination was made of it.

A sample of electrolytic oxygen was then taken from the large generator and washed in KOH and dried over P_2O_5 on glass wool. Two examinations were made, on different days, but *no* emission band could be detected at 4.75 μ. In the region of 1 μ no deflections greater than 1.5 mm. were recorded. As a whole the gas showed *no* emission lines for the region examined, which was to 5 μ, This is of considerable interest in what follows on CO and CO_2, where there is a strong emission line at 4.75 μ.

Carbon Dioxide, CO_2.

This gas was made from $KClO_3 + H_2SO_4$ and dried in P_2O_5. It was found that there are *no* emission lines until we arrive at 4.75 μ.

The current through the gas varies with the pressure. An examination of the 4.75 μ band was made for constant current and variable pressure, the current being 0.02 ampère. The results are shown in Fig. 6, which will be discussed in connection with CO, and it will be sufficient to add that the gas was first put into a pipette of phosphorus to remove the oxygen which was present. Starting with a sample of this gas at 1 mm. pressure, and adding oxygen until the pressure was 3.7 mm., no change could be detected in intensity of 4.75 μ the band which would indicate that if the band be due to CO then the CO_2 is already dissociated when starting. Occasionally a dark ring or dark patches would appear on the inside of the constricted portion of the vacuum tube. It would suddenly disappear and then reappear elsewhere. Whether it was due to carbon in the tube or to the dissociation of CO_2 remains undetermined.

Warburg's work[1] shows that the temperature of the axis of the tube is much higher for nitrogen than for hydrogen, so that traces of CO_2 in nitrogen ought to become the hotter. It was noticed that the 4.75 μ band occurring as an impurity, was most intense in nitrogen, which, if the same amount of CO_2 was present in each gas, would indicate that the N was the hotter.

Carbon Monoxide, CO.

The CO was made by heating oxalic acid, $C_2H_4O_2$, and conc. H_2SO_4 and passed through a KOH solution into a pipette of KOH. The generating flask was then replaced by a mercury gas pipette and a tube of P_2O_5 on glass wool, and the gas was then washed back and forth through the P_2O_5 for a long time. This sample showed no water vapor lines at low pressures. The emission curves of CO are in Fig. 5, where curve *a* is for a pressure of 0.3 mm. and *b* for a pressure of 0.8 mm. There seems to be a slight trace of radiation throughout the spectrum but *no* strong emission lines are to be found except the one at 4.75 μ.

An examination of this band was made for a constant current of

[1] Warburg, Ann. der Physik. (3), 34, p. 265, 1895.

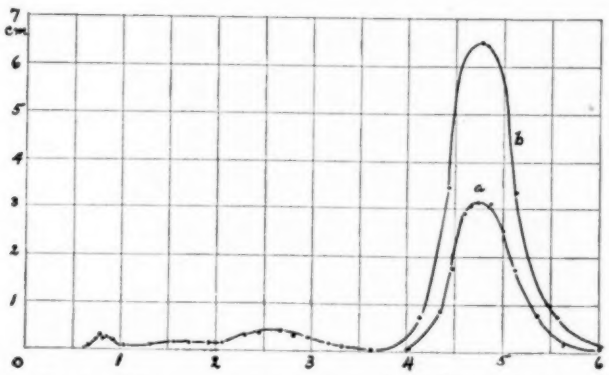

Fig. 5. CO ; $a = 0.3$ mm. pressure, $b = 0.8$ mm. pressure.

0.02 amp. and variable pressure. The results are given in Fig. 6, in which the abscissæ are pressures in millimeters of mercury, and the ordinates are deflections in centimeters. It is to be noticed that

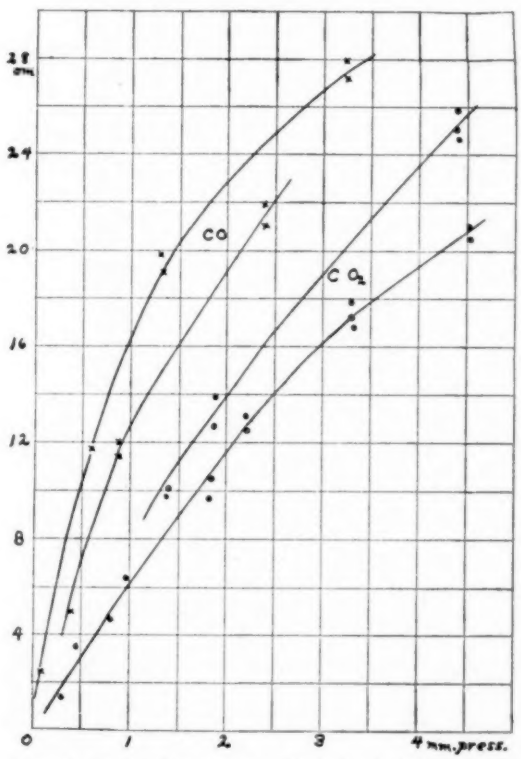

Fig. 6. CO and CO_2 band at 4.75 μ. Variation in intensity with pressure.

the intensity of the CO band is much greater than that of CO_2 for *all* pressures, the current of 0.02 amp. being the same for both gases. Moreover the intensity does not pass through a maximum as is true of the H and N lines lying near the visible spectrum. The greater intensity of the CO would make it appear as though the 4.75 μ band were due to this gas.

Ethyl Alcohol, C_2H_5OH.

Ordinary absolute ethyl alcohol was used. It was introduced into the previously exhausted pump, through an especially provided bulb and stopcock. The emission curve, Fig. 7, is very un-

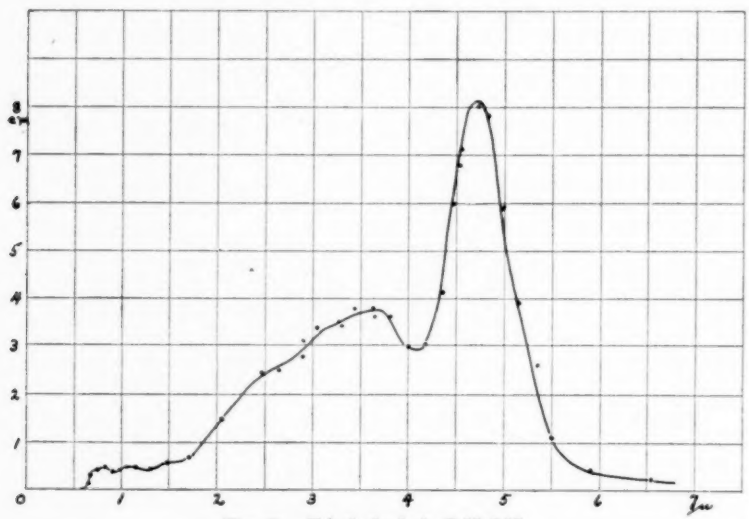

Fig. 7. Ethyl alcohol, C_2H_5OH.

usual. It shows no distinct lines except the strong band at 4.75 μ which is to be found only in CO and CO_2. The continuous spectrum from 2 to 4 μ is difficult of explanation. Possibly it is a composite of bands of alcohol vapor equivalent to the water vapor bands found in the bunsen flame. In the latter, however, the bands are in groups with regions of zero radiation. The bands at 4.75 μ indicate a dissociation of the alcohol vapor into H (red line) and CO_2 or CO, just as ammonia shows the nitrogen bands.

Nitrogen, N.

The first sample of nitrogen examined was made by heating a saturated solution of equal parts of sodium nitrite, $NaNO_2$, and ammonium chloride, NH_4Cl, washed in KOH and dried in H_2SO_4 and in P_2O_5.

The emission spectrum of this sample of N is given in Fig. 8, curve *b*. In addition to strong lines just at the end of the red we have the usual band at 4.75 μ which is unusually intense. In fact,

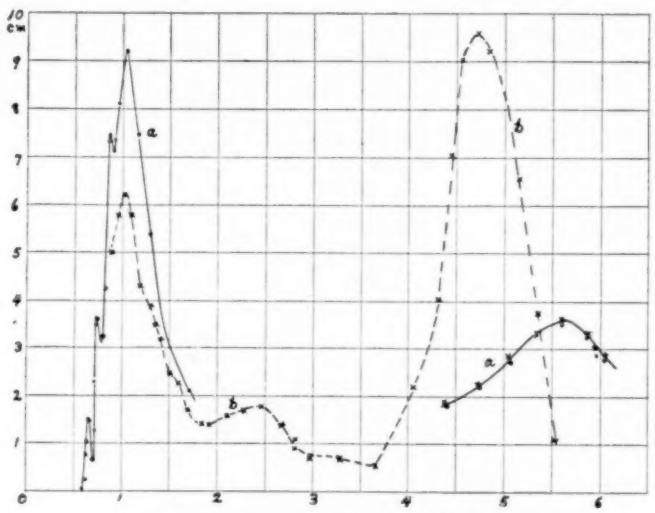

Fig. 8. Nitrogen ; a = atmospheric nitrogen.

for a pressure of 5 mm. the deflections from this band were from 30 to 35 centimeters.

One difficulty in making nitrogen by this method is that the oxides are also formed. The presence of the 4.75 μ band showed that it is due to CO_2 or traces of N in CO or CO_2. The problem then was to prepare a small quantity of nitrogen which was free from oxides of nitrogen, and also free from O and CO_2. The presence of a trace of an inert gas like helium did not enter the question of the origin of the 4.75 μ band. Hence atmospheric nitrogen was most serviceable. To this end a glass tube containing P_2O_5 on glass wool was connected in series with a gas pipette containing a strong KOH solution and a pipette containing sticks of red phosphorus under water. The phosphorus of course was used to re-

move the O, while the KOH removed the CO_2. The air was washed back and forth for some time. The KOH pipette was then replaced by a mercury gas pipette, and the gas was washed back and forth for about half an hour to dry it and remove the last traces of oxygen.

The result is shown in curve *a* of Fig. 8, which is of no small significance, especially in the region of 4.75 μ where *no band* is to be found. The curve (dots and crosses) shows that the radiation from the gas and from the hot cell is of equal intensity. The decrease in the intensity, thus forming an apparent maximum at 5.5 μ is due to the fact that in moving the spectrometer arm the vacuum tube was not adjusted before the slit, hence the last two readings are for the radiation from the side of the tube instead of its axis.

In the final work the gases were not studied in the order given here, the CO_2 and CO coming last. The absence of the 4.75 μ

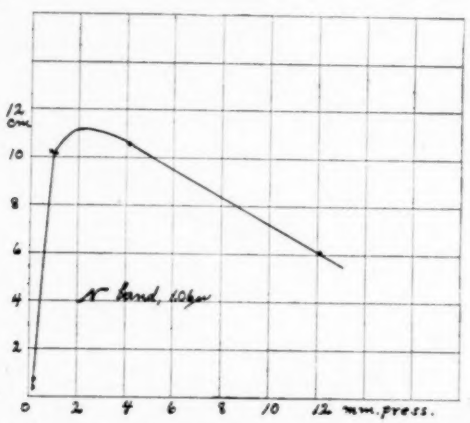

Fig. 9. Variation in intensity with pressure of the nitrogen band at 1.06 μ.

band in N and NH_3 excluded the possibility of its being due to nitrogen. Several drops of water were introduced into the gas, but no change could be detected in the radiation at 4.75 μ showing that this band is not due to water vapor. Hence it remained to be shown whether it is due to CO_2 or CO.

In discussing those two gases it was shown that the radiation from CO is much stronger than for CO_2 at 4.75 μ.

The presence of strong emission bands just beyond the red hav-

ing maxima at 0.66 μ, 0.75 μ, 0.90 μ and 1.06 μ was found only in nitrogen. Helium [1] is the only other gas known which has strong lines (bands) in this region, and from the scanty data at hand it appears as though this property were confined to the inert gases.

A study was then made of these emission bands under constant current and variable pressure and *vice versa*. In Fig. 9, is given the curve of the 1.06 μ band for variable pressure (current const. 0.02 amp.) which is the ordinary gas conduction curve of the visible spectrum. Ordinates are deflections in centimeters, abscissæ are

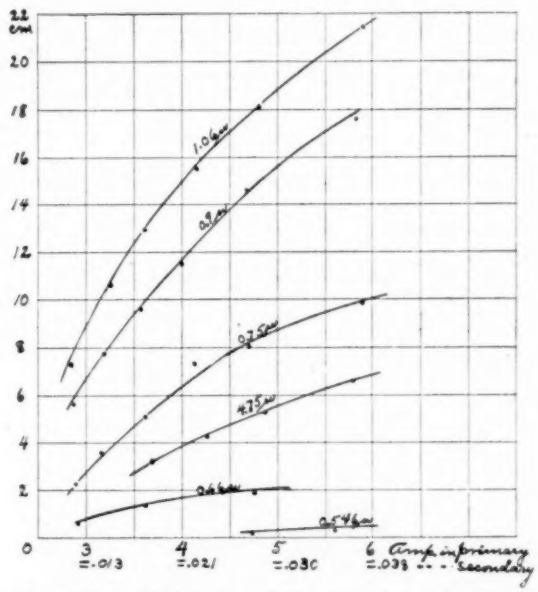

Fig. 10. Variation in intensity of the nitrogen bands with current.

pressures in millimeters. The maximum lies at about 2 mm. which agrees well with observations in the visible spectrum.

In Fig. 10 are given the emission curves of the bands at 0.546 μ, 0.667 μ, 0.75 μ, 0.90 μ, 1.06 μ and 4.75 μ, keeping the pressure constant at 1.4 mm. and varying the current.

All the curves agree in showing that the intensity (plotted as ordinates) increases with increase in current in the secondary, which agrees with Langenbach,[2] and with Ferry [3] for the visible spectrum.

[1] Runge and Paschen, Astrophys Jour., 3, p. 4, 1896.
[2] Langenbach, Ann. der Phys. (4), 10, p. 789, 1903.
[3] Ferry, PHYS. REV., 7, 1, 1898.

Several large Leyden jars were used in parallel with the vacuum tube when the intensity of the radiation increased due to an increase in the current through the tube.

Ammonia, NH_3.

The ammonia used was made by heating $NH_4Cl + KOH$ (solid) and passing the gas through tubes of CaO which had been heated for several hours. These tubes were heated while starting, to expel the air. The first sample was examined just after the C_2H_5OH, and from the appearance of the curve, Fig. 11, some of

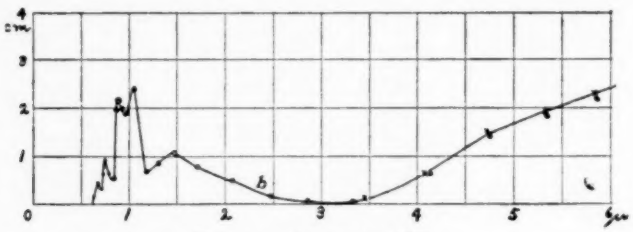

Fig. 11. Ammonia, NH_3.

the latter vapor must have been present. The second sample, made with greater precautions, did not show any radiation beyond 2.5 μ. In the region of 4.75 μ, the observations for the radiation from the hot cell and the gas (indicated by crosses) coincide. The nitrogren bands at 0.75 μ, 0.9 μ and 1.06 μ are due to the dissociated NH_3.

Radiation From a Vacuum Tube When Heated Externally.

The very different behavior of the 4.75 μ band from those at the end of the red made it highly desirable to learn whether it can be due to the mere rise in temperature of the gas. If it obeys Kirchoff's law, it cannot be more intense than the black body radiation at the same temperature. The radiation of the hot glass cell beyond 3 μ, when hot (at cathode-ray pressure) gave deflections that were comparable with that of the 4.75 μ band. This would lead one to think that the 4.75 μ band is due simply to rise in temperature of the gas. On the other hand, in the region of 1 μ the hot cell gave *no* appreciable deflections, while the gas, nitrogen, gave *strong* emission bands, which would indicate that if these emission bands

be due to a pure thermal excitation, following Kirchoff's law then the temperature of the gas must be very high as compared with that of the cell walls. The problem then was to find the radiation from the vacuum tube when heated externally to the temperature it had during the electrical discharge, which is really the black body radiation; also to find the radiation from a black body, *e. g.*, a Leslie cube, whose temperature can be quite accurately determined.

In order to determine the radiation from the vacuum tube when externally heated, the part between the electrodes was wound with an iron wire through which an electric current was passed. The walls of the tube were heated to the temperature they generally had during the electrical discharge at very low pressure. The tube was filled with air and with CO_2, and the radiation was found for *all pressures* up to atmospheric. The deflections were thrown entirely off the scale for *all* pressures for the region of 4.75 μ, hence this region of the spectrum was not explored for emission bands. This indicates an intensity of radiation several times that from the vacuum tube during the passage of the discharge. Although the ends of the tube were not hot, when heated externally, the tube is analogous to the black body. Whether or not it is entirely analogous is not of the chief importance. Its radiation was several times as intense as that from the electrically excited tube, which was the question to be answered. Whether or not the emission band at 4.75 μ is due to thermal excitation, due merely to a rise in temperature, or to electrical excitation is undetermined. The experiment shows that since its intensity is less than that of a black body, it is not untenable to consider it to be due to a rise in temperature of the gas.

But this is not a sufficient criterion for udging the quality of the radiation. One objection is that the selective emission at 4.75 μ ceases immediately after the electrical discharge ceases, which is not true of the externally heated tube. Warburg (*loc. cit.*) has shown from theoretical considerations that after the discharge ceases it requires only a small fraction of a second for the gas to assume its original temperature.

In this connection it is well to notice Paschen's[1] work on the emission of CO_2, when heated in a metal tube, also when passed

[1] Paschen, Ann. der Physik. (3), 53, p. 26, 1894.

through a coil of sheet platinum 4 cm. long, 3 mm. internal diameter, heated electrically.

He found the radiation of the 4.4 μ band of CO_2 for columns 7 cm. and 33 cm. long. The 7 cm. column behaved like a layer of infinite thickness, *i. e.*, the intensity of the emission of this wave-length is proportional to the intensity of radiation of a black body for the same wave-length and temperature. In Fig. 12, curve *b* represents the emission of the 4.4 μ band of CO_2, for a tube 7 cm. long when heated by means of a bunsen burner from 100 to 500°. In this same figure curve *c*, also due to Paschen, shows the emission

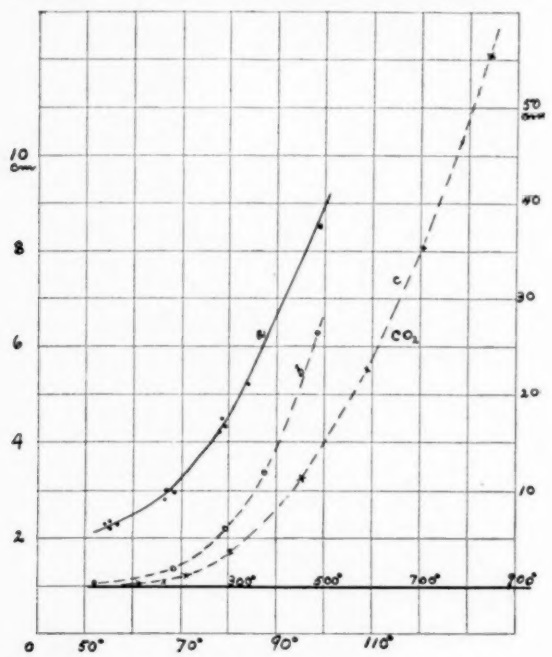

Fig. 12. Radiation from a black body at 100° C., curve *a*; curves *b* and *c* = radiation from CO_2. (Paschen.)

of the 4.4 μ band of CO_2 when heated by passing the gas through a coil of platinum which was heated electrically.

The temperature of the gas was observed by means of two thermopiles, the first one being placed at the point where the gas issued from the orifice; the second one being placed about one centimeter above this point. Both curves show the very rapid increase in intensity of the emission lines with rise in temperature.

RADIATION FROM A BLACK BODY WHEN HEATED TO 100° C.

Since the temperature of the cell could not be determined accurately it was highly desirable to compare its radiation with that of a solid whose temperature could be varied and determined more accurately. To this end the radiation from a thin-walled, blackened copper vessel was found when filled with water which was heated electrically. The escaping vapors from the hot water caused such a variation in the temperature of the room that the radiometer became very unsteady, hence only the region of 4.75 μ was examined. In Fig 12, curve *a* gives the emission curve of this vessel for different temperatures of the water. The curve is very similar to those found by Paschen. Of course, the temperature of the outside of the vessel is less than that of the water, but not sufficient to debar a comparison with the hot vacuum tube. Mention has already been made of the fact that the constricted part of the vacuum tube is the hotter at high pressures, while the regions surrounding the electrodes are the hotter at low cathode-ray pressures. At the latter pressure the deflections for the hot cell were from 8 to 10 cm. The vessel of hot water, under similar conditions gave a deflection of 8.5 cm. for a temperature of about 96°.

At a temperature of 70° the deflection is about 3 cm.

As a whole the results show that the radiation from the cell walls is due to a rise in temperature which is not much, if any, greater than that of the vessel containing water. The temperature of the gas in the vacuum tube is an entirely different question which must be considered separately.

The fact must not be overlooked that the radiation from the vacuum tube gave large deflections simply because of the great sensitiveness of the instrument and not on account of the actual intensity as compared with the deflections from gases in a Bunsen flame. In the latter the deflections for the 4.4 μ CO_2 band were some 60 to 70 cm. for the old instrument, so that in the present work the deflections would be 50 times as great, viz., 3,000 cm. In other words, in the vacuum tube curves the deflections are only from $\frac{1}{250}$ to $\frac{1}{3000}$ as great as from the bunsen flame, and the Nernst heater.

TEMPERATURE OF GAS IN THE VACUUM TUBE.

Warburg's theoretical work (*loc. cit.*) on the temperature of the vacuum tube has already been mentioned. He showed that the temperature of nitrogen is much higher than that of hydrogen.

The intensity of the 4.75 μ impurity band in nitrogen, for all pressures, was so much greater than for all the other gases that one is led to think that it is due to the higher temperature of the gas.

Wood [1] gives data from the observed mean temperature of gases in a vacuum tube for different pressures, and currents of 0.001 to 0.003 ampere. In all cases the computed and observed temperatures are in fair agreement, the observed values being slightly less than Warburg's values, as one would expect, from the use of a thermopile which cannot be made infinitely thin. The observed values fall upon a straight line, which shows the accuracy of the observations. Using these values and extrapolating to a current of 0.02 ampere, in the present work, for a pressure of 1.8 mm. of nitrogen this would indicate a temperature of about 250° C. while for a pressure of 3 mm. the temperature of the axis would be about 325°. For a current of 0.025 ampere the temperature would be 300° and 400° respectively.

The whole shows that for the large currents used in the present work (0.02 to 0.028 amp.) it is not unthinkable that the 4.75 μ band is due to the heating of the residual gas. On the other hand, the black body at 325° C. does not emit a very perceptible radiation at 1 μ while the emission lines of N in this region are very intense. They indicate a very much higher temperature, some 4000° abs., if we consider the maximum of the envelope of the curve, drawn through the highest points of these emission lines, which maximum lies just beyond the red. This reasoning leads to the result that the gas is at two distinct temperatures, which is hardly the case. If the gas had this high temperature then one would expect the cell walls to grow hotter. Electrical excitation suggests itself, which brings us to a theoretical consideration of the phenomena of vacuum tube radiation.

THEORETICAL.

It remains for us to consider the theoretical side of this subject. Experimental observations always have some value. This is not

[1] Wood, Ann. der Physik. (3), 59, p. 238, 1896.

always true of theories which are built, more or less, upon hypotheses and must stand or fall with them. For example, nowadays one no longer considers spectra to be due to molecular or atomic vibrations; the divisibility of the atom into smaller electrically charged particles, called "ions" or "corpuscles" must be assumed to account for observed facts. The foremost and most conservative in propounding such a theory is J. J. Thomson.[1] J. Stark[2] is more daring in that he classifies these "ions," and gives the functions that each class has to perform.

Before considering these theories it will be well to distinguish between several forms of radiation, since everybody gives out some form of radiation, in the form at least of heat waves of great wavelength. If a body can give out radiation continuously without changing its nature it is called a *pure thermal* radiation. If it cannot continue to give out this radiation indefinitely, without changing its nature, even when the temperature is kept constant (*e. g.*, fluorite which emits light on heating) then the radiation is termed *luminescence.* The vacuum tube is thought to give out light by "*electro-luminescence.*"

The vacuum tube is always quite cool in comparison with the arc. This brings us to the question of "temperature." What do we mean by the temperature of a body, particularly with the two forms of radiation just mentioned. Both emit light, nevertheless, if we were to heat a piece of iron until it felt as hot to the touch, or until the mercury in a thermometer expanded to the same height, as it does for the vacuum tube, we know from ordinary experience that the iron would not emit light. "Temperature" is something we are supposed to measure by ordinary means. The word itself is used carelessly and is an endless source of discussion. To anticipate a little what is to follow — Stark uses the terms "thermal and electrical temperature." The purely "*thermal temperature*" for any one gas is proportional to the mean square of the *molecular* speeds. The "*electrical temperature*" is proportional to the mean square of the *ionic* speeds. In a strong electrical field, *e. g.*, spark electrodes, the ionic velocities will be distributed in a very different

[1] Thomson, Conduction of Electricity Through Gases, Chaps. 13 to 16.
[2] Stark, Elektricität in Gasen.

manner from that prescribed by the Maxwell-Boltzmann Law, and the "electrical temperature" may differ very widely from the "*thermal.*" The arc is a region of high thermal and low electrical temperature; the spark has a low thermal and a high electrical temperature.

To return to the theory, there is considerable evidence for believing that the chemical atom or molecule is composed of positively and negatively charged particles called ions. These oppositely charged particles are equal in amount since the molecule as a whole is electrically neutral. It is possible to separate from the molecule a minute particle which carries a negative charge, and thus leave an equal positive charge on the remainder of the molecule. This state of affairs is brought about whenever an electric field is produced, as for example, the difference of potential between the terminals in the carbon arc, of the spark gap in the secondary of an induction coil, or of the electrodes of a vacuum tube. Under the influence of an electric field these dissociated particles are set in motion. Beside their ordinary gas motion, there will be a component along the length of the tube (in a vacuum tube) produced by the electrical forces. Although the charges are the same, the negative ions, the electrons, on account of their small mass will acquire a great speed, and by collision with neutral molecules will give rise to fresh ions. The energy acquired however will be the same for both since they move through the same difference of potential. The mean free path of the electron will be the greater since it is smaller in size. The mean energy at collision, in any case, will be that acquired by the charged particle in moving through its path under the action of electrical forces. When the electron collides with a molecule several effects will be produced. The first is to increase the kinetic energy of the molecule as a whole, which in turn by colliding with other molecules, will cause a rise in the thermal temperature of the gas. As a result the electrons in the molecules will be thrown out of their positions of equilibrium and will execute a series of vibrations. In so doing they will emit radiation in the form of heat or light, depending upon the intensity of the excitation, which in turn depends upon the temperature.

When an electron collides with a molecule the second effect is an acceleration of the former, which, when properly interpreted, means a wave motion, hence periodicity (Stark, *loc. cit.*). This period will be determined by the time of impact, independently of the chemical nature of the body. Since all possible times of impact are possible, an infinite number of different electromagnetic waves will be emitted, and we have a continuous spectrum. This is for the free electrons. The electrons that remain bound in the molecule will also be set into vibration by the impact of the collision. Since they are thus bound, there will be a relative motion among them, and the period of any one or group of these electrons will be characteristic of the kind of atom. The line and band spectra of the elements are, from this standpoint, due to these electrons within the atom.[1] In a more recent paper on tnis subject by Nutting,[2] the recombination of these dissociated aggregates is emphasized as being the source of line spectra.

For this second effect the energy increases with the potential gradient, since the radiation from the gas is caused by the collisions between molecules and electrons, which latter are moving with high speeds. As already mentioned in the high temperature radiation, where the collision is between molecules, the energy increases with the temperature. The electrical temperature distribution will be different from the thermal, and Kirchoff's law for the relation between emission and absorption will not hold for radiation from a gas in a vacuum tube. The spectral distribution of intensity will be a function of the velocity distribution of the electrons. The greater the number of electrons with high speed in a volume element, the more will the intensity maximum be shifted towards the short wavelengths.

For this reason the cathode glow is blue, since the cathode fall is about 300 volts. On the other hand in the position column, where the fall is only about 30 volts, the light emitted is red for nitrogen. According to Stark's (*loc. cit.*) computations in which the kinetic energy is equated to the temperature, this would indicate an electrical temperature of some 6000° for the cathode glow.

[1] Stark, Ann. der Phys. (4), 14, p. 506, 1904.
[2] Nutting, Astro. Phys. Jour., 21, p. 400, 1905.

The ionic energy[1] (the minimum kinetic energy) necessary to disrupt an atom is in the order, metals, Hg 8 (volts), H, N (27 volts) and O. From this it would follow that if we mix H with N the fall of potential and the electrical temperature of the positive column will be changed. The temperature will be increased if the gas to be added has a higher ionic energy, *e. g.*, N to Hg or N to H (Heuse,[2] Herz). This will be of interest in comparing the relative intensities of the 4.75 μ band of CO_2 when it occurs as an impurity in N (very intense) and in O or NH_3 where it is weak.

These views will now be briefly considered in connection with the results obtained in the present research.

Prior to this investigation on vacuum tube radiation only one type of selective emission of gases in the infra-red had to be accounted for, viz., emission bands of water vapor and CO_2. They were thought to be due to thermal temperature of the gas. However, the data bearing upon this subject are so scarce that writers, in referring to them, generally expressed their opinions rather cautiously. Some have vaguely intimated that it might be something similar to luminescence in the visible spectrum — call it thermalescence.

From the present research on the intensity of the infra-red emission bands of N and CO_2, for constant current and varying pressures, and *vice versa*, it becomes evident that we have to deal with two distinct types of radiation, the one being represented by the 4.75 μ band of CO and CO_2, the other being represented by lines of N at 0.90 μ and 1.06 μ. The 4.75 μ band of CO and CO_2 behaves in an entirely different manner from all the rest. Its intensity increases with increasing pressure (for constant current) of the gas, but never reaches a maximum, becoming asymptotic at 5 to 6 mm. pressure.

On the other hand, the other bands increase in intensity with increase in pressure (for constant current), become a maximum at about 2 mm. pressure, and then decrease in intensity with a further increase in pressure, which agrees with observations in the visible spectrum.

All lines increase in intensity with increase in current, as found in the visible spectrum.

[1] Herz, Ann. der Phys. (3), 54, p. 244, 1893.
[2] Heuse, Verh. d. d. phys. Ges., 1, 269, 1899.

Condensers in parallel with the vacuum tube caused a slight increase in the intensity of the lines, due to an increase in the current through the tube. This is due to the well known fact that on account of the high self-induction of the coil, the discharge of the condenser takes the easier path through the vacuum tube. The whole shows that the bands of N, (He), and H, near the visible spectrum, are related to the visible bands, while the 4.75 μ band is of an entirely different type.

Returning to the theory, it is interesting to recall Ångström's [1] predictions in regard to the mechanism which produces these radiations. As noticed elsewhere, he found that the total radiation *increases*, while the luminous radiation *decreases* with increase in pressure of the gas, and concluded that there is a "regular" and "irregular" radiation present during the electrical discharge. This would tend to change the efficiency of the vacuum tube, as found by Ångström and by Drew.

In the present work, the *decrease* in infra-red radiation (4.75 μ band) and the simultaneous *increase* in the visible radiation, with decrease in pressure, explains very clearly the rise in efficiency of vacuum tubes. It also explains why the total radiation passes through a minimum as observed by Ångström and by Drew (*loc. cit.*).

In connection with the theoretical work just mentioned the behavior of these two types of radiation may be explained in the following manner: Consider the lines in and near the visible spectrum. At high pressures the electrons will not attain a high speed on account of the numerous neutral molecules, and their freedom of motion will be limited. At a lower pressure their freedom of motion will be greater, the number of collisions will be more frequent, the ionization will increase and the electrical temperature [2] which is proportional to the mean square of the ionic speeds will attain a maximum. At a still lower pressure, on account of the scarcity of the molecules, there will be fewer collisions in a given time, the ionization will decrease and the "electrical temperature" will decrease.

On the other hand this explanation will not account for the behavior of the 4.75 μ band which appears to be due to a thermal

[1] Ångström, Ann. der Physik. (3), 48, p. 493, 1893.

[2] Stark, Elektricität in Gasen, from consideration of the kinetic energy of the electron computes an electrical temperature of some 6000°.

radiation, excited by the collision of electrons with the neutral gas molecules. The gas molecule as a whole will suffer an increase in its kinetic energy, and, in colliding with other molecules, will cause a rise in the thermal temperature of the gas. With increase in pressure, *i. e.*, in the number of gas molecules, the number of collisions will increase, the intensity of the thermal radiation will increase but will not pass through a maximum, as is true of the other bands, because a stage will be arrived at where there will be a decrease in the ionization and in the collisions of the molecules. At still higher pressures the gas would cease to conduct the current.

Aside from these theoretical considerations, there is some experimental evidence for believing that the 4.75 μ band is of thermal origin. First, the gas must be hotter than the tube, for during the passage of the current the radiation tangential to the axis of the tube is probably different from the longitudinal, and the cell walls assume the mean temperature of the gas only after the current has passed for some time. It has already been shown under the discussion of the temperature of the gas in the vacuum tube, that the mean thermal temperature is from 300° to 400° C., depending upon the current and the pressure. It was also shown there that the black body at these temperatures did not emit a perceptible radiation at 1 μ, while the emission lines in this region are very intense, indicating a temperature of perhaps 4000° abs. On the other hand the "black body" at 4.75 μ radiated almost as intensely as the vacuum tube. This would indicate two distinct temperatures, which is hardly the case.

Second, the distribution of the heat in the vacuum tube is very different for different pressures. At a high pressure the constricted portion of the vacuum tube is the hotter while at low pressure it is quite cool, and the region surrounding the electrodes is the hotter.

Third, the emission increases with the pressure (equivalent to an increase in the thickness of the emitting layer) and approaches a limiting value. Paschen (*loc. cit.*) has found for CO_2 at atmospheric pressure, in a brass tube heated by a bunsen burner that a column 7 cm. long emitted and absorbed energy just as strong as a column 33 cm. long. In the present case the 15 cm. column of CO_2 at 5 mm. pressure is equivalent to a column 1 mm. long at 760 mm.

pressure. This is not a very long column of the gas as compared with Paschen's, nevertheless, judging from the behavior of the small traces of CO_2 in air, it does seem impossible for it to emit radiation as intense as that observed at 4.75 μ. This would require a very high temperature. If the shifting of the CO_2 band toward the long wave-lengths continues with the rise in temperature for the region beyond 4.4 μ, just as Paschen (*loc. cit.*) found for the region preceding 4.4 μ, then the 4.75 μ band would indicate a temperature of some 6500° to 7000° (found by extrapolating from Paschen's values). This is close to Stark's (*loc. cit.*) "electrical temperature" of 6000° for the cathode glow. Returning to the strong emission lines just at the end of the red, if we consider the maximum of the envelope (the curve) drawn through the highest points on these emission lines, which maximum lies just beyond the red, then, from the "displacement law" $\lambda_{max.} T = \text{const.}$, the thermal temperature appears to be about 4000° abs.

From this line of reasoning it would appear that we can consider the 4.75 μ band and the bands at the end of the red to be due to a high thermal condition in the vacuum tube, without having recourse to an "electrical temperature."

The continuous spectrum of alcohol vapor would indicate a higher temperature than that found by bolometric measurements. But even here the evidence is contradictory when compared with the emission of water vapor which showed no emission spectrum at 2.8 μ, where the bunsen flame has emission lines.

Evidently further investigation is needed to elucidate this subject — and such an investigation is in progress.

Summary.

The present investigation of infra-red emission spectra had for its aim the study of the region of the spectrum lying beyond 2 μ, which heretofore had never been examined. The question of the presence of emission lines beyond this point is chiefly of theoretical interest.

Two classes of radiation have been investigated, viz., the arc between metallic electrodes and the chlorides of the alkali metals in the carbon arc, and the discharge through a vacuum tube using different vapors and gases.

It was found for the arc between metal electrodes, that the oxides emitted a black body spectrum of sufficient intensity to obliterate any emission lines if any were present.

Using the chlorides of the alkali metals, the strong emission lines mapped by Snow were verified, but beyond $2\,\mu$ *no* emission lines could be found.

The emission spectra of the following vapors and gases were examined in a vacuum tube; H_2O, C_2H_5OH, H, N, NH_3, CO and CO_2. Of this number the C_2H_5OH, CO_2 and CO have a very strong emission band at $4.75\,\mu$.

Nitrogen is the only gas studied which has strong emission lines in the infra-red. The maxima are at $0.75\,\mu$, $0.90\,\mu$ and $1.06\,\mu$. The behavior of these lines is entirely different from the $4.75\,\mu$ band found in CO_2 and CO. At a constant current the intensity of the $4.75\,\mu$ band increases with the pressure but never reaches a maximum, becoming asymptotic at 5 to 6 mm. pressure. On the other hand the nitrogen bands increase in intensity with increase in pressure, become a maximum at about 2 mm. pressure, then decrease in intensity with a further increase in pressure, which agrees with observations in the visible spectrum.

At a constant pressure all lines increase in intensity with increase in current, as found in the visible spectrum.

Condensers in parallel increased the intensity slightly, due to an increase in the current through the tube.

The aim in using a vacuum tube was to avoid oxides. No lines, however, were found beyond $2\,\mu$, except the $4.75\,\mu$ band which seems to be due to the warming of the gas. Since the intensity of the vacuum tube radiation is only from $\frac{1}{2\,6\,0}$ to $\frac{1}{3\,0\,0\,0}$ as great as that of a black body, if there be weak emission lines beyond $6\,\mu$ it would be almost impossible to detect them with our present measuring instruments.

The emission spectrum of C_2H_5OH shows that a vapor in a vacuum tube can emit a continuous spectrum.

BUREAU OF STANDARDS,
WASHINGTON D. C., Aug., 1905

THE EQUAL ARM BALANCE.

By H. V. Carpenter and Zella E. Bisbee.

THE static equations of the balance have been worked out in a variety of forms depending upon the completeness with which the errors of the construction are taken into account. It was the purpose of this investigation to determine the value of the constants in these equations for balances of common types, in order that the equations might be reduced to the simplest form that would represent the true conditions. The equation of equilibrium of the balance to be sufficiently complete must be one which expresses the state of the balance under all conditions of load, sensitiveness, and rigidity of the beam. The formulæ given here were worked out with this end in view, and have been carefully checked experimentally to show the values of the constants involved and to determine how closely the theoretical conditions are fulfilled by the balances in use. In order to secure the most satisfactory experimental check the general equation of equilibrium derived below was placed in such a form that it expressed the sensitiveness of the balance as a function of the load upon the pans.

Derivation of the General Equation of Equilibrium.

The discussion which follows is based upon the following statements:

1. The inequality of the arms is so small that it may be neglected. It rarely exceeds .01 per cent. and so while it must be considered for accurate weighing it is not appreciable in the mechanical behavior of the balance.

2. The knife edges in a satisfactory balance are so thin that their thickness may be neglected except possibly for very sensitive conditions of the balance. This was tentatively assumed and is borne out by the experimental results which are given.

3. Since all readings of the deflection of the beam are taken with

the beam stationary or by an equivalent method, the center of mass of each pan with its stirrup and load may be taken as always exactly beneath its supporting knife edge and no effect would be produced on the behavior of the balance if the mass of each pan with its stirrup and load were concentrated at its supporting knife edge.

4. Any load added to the pans will cause a downward distortion of the beam with a consequent lowering of the end knife edges and of the center of gravity of the beam. The experiments show the magnitude of this effect.

5. The line joining the center of gravity of the beam with the central knife edge is assumed to be perpendicular to the straight line joining the end knife edges. This condition is always very closely approached in the ordinary adjustment of the balance, and

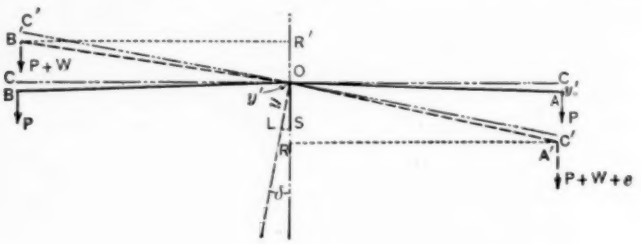

Fig. 1.

any ordinary error in it would not appreciably affect the behavior of the instrument.

Since each pan with its load may be considered as having its center of gravity at its knife edge, we may treat the two as acting together at a point half way between the two knife edges, that is at a point directly below (or above) the central knife edge as indicated in Fig. 1. Distances downward are considered as positive and distances upward as negative.

Let O = central knife edge.

P = mass of one pan and stirrup.

e = excess weight.

$OA = OB = OA' = OB' = l$, the length of each arm.

B = mass of beam.

W = load on one pan.

v_0 = distance of the center of gravity of beam below O, with pans empty.

y_0' = distance of the effective center of gravity of pan system above or below O, with pans empty.

$\bar{y}_0$ = distance of the center of gravity of entire moving system below O with pans empty.

Since any distortion of the beam due to added weights in the pans will be proportional to the weights added we can write $OL = y = y_0 + KW$, where y is the distance the center of gravity of the beam lies below O for the load W grams in each pan, and K is the increase in y due to one gram increase in W. Similarly $A'C' = y' = y_0' + K'W$ where K' is the distance the end knife edges are lowered by 1 gram increase in each pan. K' will always be larger than K.

Now from the law of moments,

$$B \cdot LS + (P + W)B'R' = (P + W + e)A'R, \qquad (A)$$

$$\sphericalangle COC' = \sphericalangle LOS = \delta$$

and

$$\sphericalangle A'OC' = \sphericalangle B'OC' = \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)$$

$$= \cos^{-1}\frac{\sqrt{l^2 - (y_0' + K'W)^2}}{l}.$$

$$\therefore \sphericalangle OA'R = \sphericalangle COA' = \sphericalangle COC' + \sphericalangle C'OA'$$

$$= \sphericalangle \delta + \sin^{-1}\left(\frac{y_0' + K'W}{l}\right).$$

Likewise

$$\sphericalangle B'OC = \sphericalangle \delta - \sin^{-1}\left(\frac{y_0' + K'W}{l}\right).$$

Then

$$B'R' = l\cos\left[\delta - \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right],$$

$$LS = y\sin\delta = (y_0 + KW)\sin\delta,$$

$$A'R = l\cos\left[\delta + \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right],$$

and equation A becomes

$$B\sin\delta(y_0 + KW) + (P + W)l\cos\left[\delta - \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right]$$

$$= (P + W + e)l\cos\left[\delta + \sin^{-1}\left(\frac{y_0' + K'W}{l}\right)\right],$$

$$B \sin \delta(y_0 + KW) + (P + W)l \left\{ \cos \left[\delta - \sin^{-1} \left(\frac{y_0' + K'W}{l} \right) \right] \right.$$

$$\left. - \cos \left[\delta + \sin^{-1} \left(\frac{y_0' + K'W}{l} \right) \right] \right\} = el \cos \left[\delta + \sin^{-1} \left(\frac{y_0' + K'W}{l} \right) \right],$$

$$B \sin \delta(y_0 + KW) + (P + W)l \left\{ 2 \sin \delta \left(\frac{y_0' + K'W}{l} \right) \right\}$$

$$= el \left[\cos \delta \frac{\sqrt{l^2 - (y_0' + K'W)^2}}{l} - \sin \delta \left(\frac{y_0' + K'W}{l} \right) \right].$$

$$B \sin \delta(y_0 + KW) + (P + W) 2 \sin \delta(y_0' + K'W)$$

$$= el \cos \delta \frac{\sqrt{l^2 - (y_0' + K'W)^2}}{l} - e \sin \delta(y_0' + K'W),$$

$$\sin \delta [B(y_0 + KW) + 2(P + W)(y_0' + K'W) + e(y_0' + K'W)]$$

$$= el \cos \delta \frac{\sqrt{l^2 - (y_0' + K'W)^2}}{l}$$

Since a balance will not work satisfactorily if y_0' exceeds .01 cm. and K' in the balance having the most flexible beam of any tested had a value of .0001, it will be seen that $(y_0' + K'W)^2$ is negligible as compared with l^2 and $e(y_0' + K'W)$ is so small in comparison with $2(P + W)(y_0' + K'W)$ that the equation takes the form

$$\tan \delta = \frac{el}{(yB_0 + KW) + 2(P + W)(y_0' + K'W)}. \qquad \text{(I.)}$$

The above equation may also be derived more directly as follows, making the same approximations as in the formula above.

$$\bar{y}_0 = \frac{\Sigma My}{\Sigma M} = \frac{By + 2(P + W)y'}{B + 2(P + W)} = \frac{B(y_0 + KW) + 2(P + W)(y_0' + K'W)}{B + 2(P + W)}.$$

Suppose the addition of a small weight e to one pan causes a steady deflection δ of the system. The weight e will cause a moment in one direction of $el \cos (\delta + < A'OC')$ equaling closely $el \cos \delta$. The restoring moment due to the deflection of the beam will be

$$[B + 2(P + W)] \bar{y}_0 \sin \delta,$$

so for equilibrium

$$[B + 2(P + W)] y_0 \sin \delta = el \cos \delta,$$

or

$$\tan \delta = \frac{el}{B(y_0 + KW) + 2(P + W)(y_0' + K'W)}. \qquad \text{(I.)}$$

Tan δ is proportional to the number of divisions deflection of the pointer, so if the excess weight, e, be taken as constant, δ and W are the only variables and the sensitiveness for different values of the load may be calculated if the constants are known. In other words it is an equation for the curve of sensitiveness of any balance.

Examination of the equation brings out the following points most of which are familiar:

1. The deflections of the pointer will be directly proportional to the difference between the loads.

2. If other things could be kept constant the sensitiveness would be proportional to the length of the beam, $2l$; for a beam of given shape however, an increase in l will cause an increase in B, or K and K', or all. The additional fact that a long beam vibrates too slowly leads makers to make the beam as short as the convenient arrangement of the pans will permit.

3. Unless the beam is very rigid and y_0' very small the mass of the pans may cause as great a decrease in the sensitiveness of the balance as the mass of the beam, further than this, the mass of the pans has a very much greater effect upon the period of vibration of the balance than the mass of the beam since the pans are farther from the center of oscillation. It is not uncommon to find balances with pans much heavier than necessary while the beam is carefully made rigid and light.

4. The balance will remain stable so long as the denominator of the fraction is a positive quantity, so either y_0 or y_0' may be negative, that is either the center of gravity of the beam or the effective center of gravity of the pan system may be above the central knife edge and still the balance may work properly.

It was found that in short beams of the common high truss type, the bending under load was too small to be detected or K and K' are negligibly small for this important class of balances; this gives us the simpler relation,

$$\tan \delta = \frac{el}{By_0 + 2(P + W)y_0'} \qquad \text{(II.)}$$

If $y_0' = 0$, or the knife edges are in the same plane,

$$\tan \delta = \frac{el}{By_0} \qquad \text{(III.)}$$

or the sensitiveness is constant for all loads.

If y_0' is positive an increase of load will decrease the sensitiveness for all values of W.

If y_0' is negative the sensitiveness will increase with the load until, when $By_0 < 2(P + W)y_0'$, the balance will be unstable.

Short beam balances are commonly sent out by the makers with the end knife edges slightly below the central one. There are two reasons for this :

(1) Such a balance will weigh light bodies with greater accuracy than heavy ones, which is usually desirable. (2) A heavy body balanced in the pans increases the moment of inertia of the system greatly, but if it decreases the sensitiveness at the same time the period of swing may not be much changed.

The condition giving constant sensitiveness is very desirable since it enables weighings to be made by interpolation with great rapidity but it is very difficult to adjust the balance to this condition.

In the case of long or slender beam balances that will bend enough under load to effect their behavior, if y_0' is positive the sensitiveness will decrease as the load increases more rapidly than it would if the beam were rigid. If y_0' is negative, we have the interesting case in which as the load is increased, the sensitiveness rises at first, possibly to infinity, and then as the effect of the bending of the beam becomes greater the sensitiveness will decrease. This may be understood by giving y_0' a negative value in equation I.

$$\tan \delta = \frac{el}{B(y_0 + KW) + 2(P + W)(y_0' + K'W)}.$$

As W increases the denominator will decrease at first and then increase, reaching a minimum value and causing a maximum value of $\tan \delta$ at the value

$$W = -\frac{2y_0' + 2PK' + BK}{4K'},$$

an expression which increases with the negative value of y_0', and

which can be shown to be a load less than half great enough to bring the knife edges to the same plane. If y_0' is not very small the value of W for maximum sensitiveness may be greater than the capacity of the balance as determined by the safe load of the knife edges, in which case the sensitiveness would increase with the load throughout or it might reach infinity within the limit of the balance.

The experimental work was taken up to see first, whether or not the equations as given are sufficiently complete and accurate; second, to determine the value of the constants in the equations for the balances used.

The first balance used was one listed by Queen & Co. as "Analytical Balance, No. 1," built for a capacity of 200 gr. The beam is made of aluminum, strongly braced and weighs 84.2 gr.; the

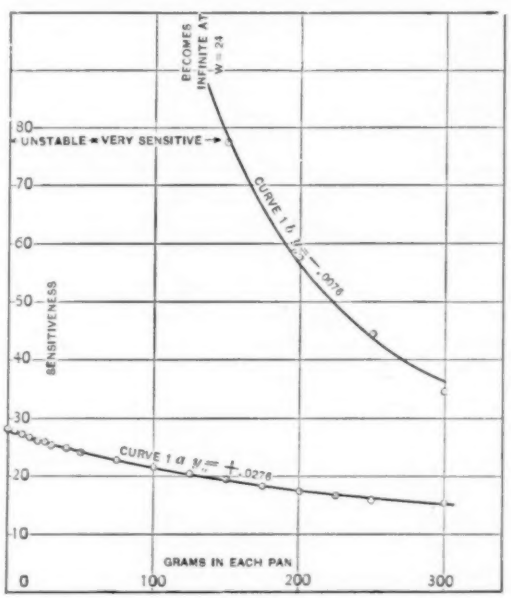

Fig. 2.

length of each arm is 7 cm. The end knife edges are each set in a brass block which is clamped in place in a slot in the beam by means of four set screws. The height of the knife edges can be adjusted by inserting pieces of paper of varying thicknesses under the brass blocks. Great care was necessary in adjusting them, however, since each knife edge must be maintained parallel to the central one.

Before any change was made in the adjustment of the knife edges, curves of sensitiveness were determined for two positions of the bob which controls the center of gravity of the beam. The values obtained are tabulated in Table I. and plotted in Fig. 2.

TABLE I.

Formula II. $\tan\delta = \frac{el}{By_0 + 2(P+W)y_0'}$. $l = 7$ *cm.* $e = .01$ *gr.* $P = 59.1$ *gr.* $B = 84.2$ *gr.* $\tan\delta = .000918d$. $y_0' = +.00385$ *cm.* I*a*, $y_0 = +.0276$.

Load in Grams.	Deflections = d		Load in Grams.	Deflections = d	
	Observed.	Calculated.		Observed.	Calculated.
− 59	36.3		40	24.8	
− 42	33.5		50	24.1	24.2
− 32	31.9		75	22.8	
− 22	30.8		100	21.5	21.5
0	27.9	27.6	125	20.3	
5	27.7		150	19.4	19.4
10	27.0		175	18.2	
15	26.5		200	17.4	17.7
20	26.2		225	16.8	
25	25.8		250	16.0	
30	25.3		300	15.1	15.0
		I*b*, $y_0 = -.0076$ *cm.*			
24		infinite	200	57.5	56.5
35	infinite	953.0	250	44.2	43.8
150	77.8	78.6	300	34.4	36.0

In all the curves given the points are experimental values while the curves are drawn to represent the theoretical values which are also tabulated. After considerable experimental work had been completed, it was found that with this balance the bending of the beam could not be detected so that formula II. represents the behavior within the limits of accuracy attained in the experiments.

In formula II.,

$$\tan\delta = \frac{el}{By_0 + 2(P+W)y_0'},$$

we have the following values: $l = 7$ cm., $e = .01$ gr., $P = 59.1$ gr., $B = 84.2$ gr. and $\tan\delta = .000918d$, where d is the deflection of the pointer of the balance in scale divisions as tabulated. This leaves the constants y_0 and y_0' to be determined by Least Square adjust-

ment. This was done using values from table I*a* and the most probable values of y_0 and y_0' were found to be $y_0 = +.0276$ and $y_0' = +.00385$ that is the center of gravity of the beam was .0276 cm. below the central knife edge and the plane of the end knife edges was .00385 cm. below the same line. Using these values and various values of W in (II.), the theoretical values given were found and are represented by the curve I*a*. The close agreement of the experimental and theoretical values throughout the range given shows simply that formula II. with proper constants represents satisfactorily the behavior of the balance for this particular adjustment throughout the entire range of load.

The next step was to increase the sensitiveness by raising the bob. This change will effect formula II. only by changing y_0, so if the actual change in y_0 can be determined experimentally, the formula should give the new curve of sensitiveness with no further change. The change in y_0 was determined as follows: The beam with the bob weighed 84.2 gr., the bob weighed 11.6 gr., the pitch of the screw carrying the bob was .0285 cm. The bob was raised a known number of turns and so an accurately known distance, then the change in y_0 is equal to the change in the position of the bob multiplied by the ratio of the mass of the bob to the mass of the beam and bob.

In this case y_0 was decreased .0352 cm., thus raising the center of gravity of the beam from .0276 cm. below O to .0076 above or $y_0 = -.0076$ cm. Using this value of y_0 and the previously determined value of y_0' the values given in table and curve I*b* were calculated. Experimentally, the balance was unstable until a load of 35 gr. was added and was so sensitive throughout the entire range that the determinations were very difficult. The close agreement between the calculated and experimental values here gives stronger proof that the formula is sufficient. It should be noted however, that the formula gives indifferent equilibrium at $W = 24$ gr. while the experiments show that the balance is not stable until W is greater than 35 gr. The uncertainty of the balance as the unstable condition is approached, indicates that the thickness of the knife edges is affecting its behavior.

The next step was to raise the end knife edges by placing under

them a bit of paper. It was found impossible to get the change in y_0' by measuring the thickness of the paper before inserting it, because it was impossible to tell how hard the oblique clamping screws pressed the knife edge block down upon the paper, and as there were always three or four thicknesses of paper under the knife edge block, its effective thickness could only be approximated.

The end knife edges were raised approximately .0147 cm. above their former position and curves were determined for three positions of the bob giving the data in Table II. The theoretical curve 2*a* was determined from formula II. by adjustment as before, y_0 being found to be + .0483 and y_0' — .00965. Curves II*b* and II*c* were calculated by using the same value of y_0' and correcting y_0 according to the known change of the bob as before; y_0 being equal to .0679 in II*b* and .0955 in II*c*. These curves show the entirely different behavior of the balance when the end knife edges are higher than the central knife edge. The close agreement between observed and calculated values shows that formula II. is sufficient.

TABLE II.

Formula II. $\tan \delta = \frac{el}{By_0 + 2(P + W)y_0'}$. $l = 7$ *cm.* $e = .01$ *gr.* $P = 59.1$ *gr.* $B = 84.2$ *gr.* $y_0' = -.00965$. II*a*, $y_0 = +.0483$.

Load in Grams.	Deflections.		Load in Grams.	Deflections.	
	Observed.	Calculated.		Observed.	Calculated.
— 42	20.5		50	37.8	38.7
0	26.4	26.0	75		51.5
25		31.1	100	78.1	76.2
		II*b*, $y_0 = +.0679$.			
0	16.8	16.6	100	29.1	28.7
25	18.26		150		45.3
50	20.4		200		106
75	24.5				
		II*c*, $y_0 = +.0955$.			
0	11.15	11.08	100	16.3	15.9
25		11.9	150		19.05
50		12.85	200	25.2	25
75		14	300		68.6

Several adjustments of the knife edges were made in the attempt to bring them all into one plane in order to check formula III., but without entire success. The best result is given in Table III. and curve III., Fig. 4, where, although the balance was quite sensitive,

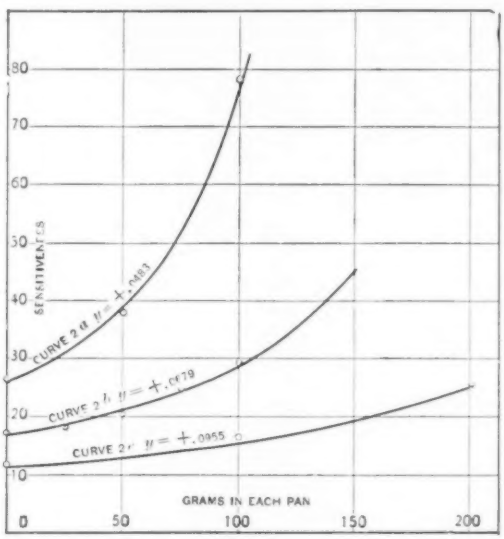

Fig. 3.

the sensitiveness varied but 5 per cent. within the limit of the balance. As this data gives .00013 cm. as the probable value of y_0', the difficulty of a closer adjustment can be appreciated. No deflections were calculated from this data.

TABLE III.

Load in Grams.	Observed Deflections.	Load in Grams.	Observed Deflections.
0	34.4	300	32.2
100	32.2	400	32.7
200	33.2		

The experiments described above made it clear that with this short, strongly trussed beam the bending of the arms is negligible with any load the knife edges should carry. In order then to check formula I. a balance having a long unbraced beam was used. It was a cheap one with steel knife edges riveted in a brass beam made by Troemner. It was found with its end knife edges below

the central one and was very carefully bent upward until the end knife edges were slightly higher. This it was found gave the desired case of a curve which has a maximum value within the range of load.

The data in tables IV*a* and IV*b* plotted with curves IV*a* and IV*b* gives its behavior under two degrees of sensitiveness. As before the curves are plotted from formula I. using adjusted values determined

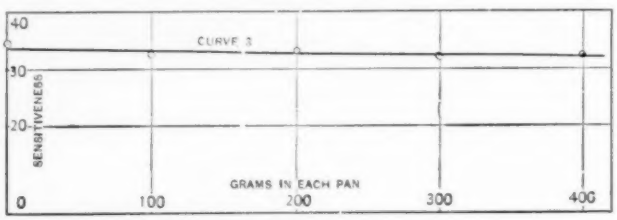

Fig. 4.

from the data in table IV*a* while the points give the observed values. Curve IV*b* is obtained by changing the value of y_0 only, the change being experimentally determined as before. The beam weighed 54.53 gr., each pan with its stirrup 43.21 gr., length of each arm 10 cm. If we collect the constants of equation I. with regard to powers of the variable W, we have

$$\frac{\epsilon l}{\tan \delta} = [By_0 + 2Py_0'] + [BK + (y_0' + 2PK')]W + K'W^2.$$

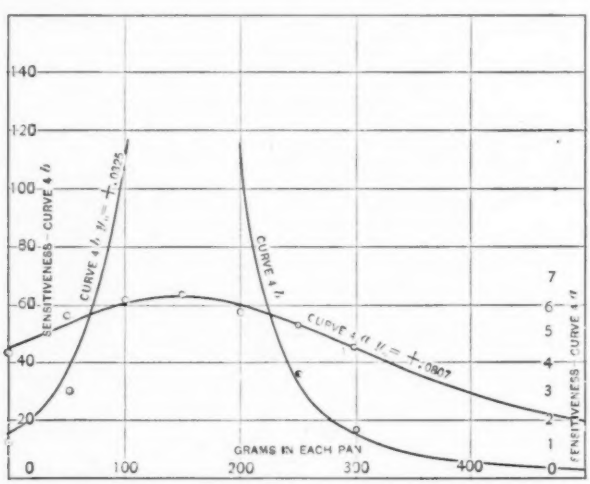

Fig. 5.

In which y_0, y_0', K and K' are unknown quantities. These unknowns are so related that the least square adjustment will not give values for all without some further relation between them. The relation of K to K' could be calculated if the beam were of simple shape and can be estimated closely enough to give good values for the others in any case, because K is of relatively small importance in the equation. In the balance used the maximum error that would be caused by omitting K entirely is 5 per cent. The solution may also be reached by determining y_0 experimentally and then solving for the others. But since y_0 is generally large as compared to y_0', this would lead to inaccurate results. K' can be determined

TABLE IV.

Formula I. $\tan\delta = \dfrac{el}{B(y_0 + KW) + 2(P+W)(y_0' + K'W)}$. $l = 10\,cm.$ $B = 54.53$ $gr.$ $P = 43.21\,gr.$ $y_0' = -.00824.$ $K = .0000054\,cm.$ $K' = .0000238\,cm.$ $e = .01\,gr.$

IV*a*. $y_0 = +.0807\,cm.$

Load in Grams.	Deflections.		Load in Grams.	Deflections.	
	Observed.	Calculated.		Observed.	Calculated.
0	4.35	4.51	250	5.3	5.30
50	5.65	5.35	300	4.5	4.47
100	6.15	6.05	400		2.94
150	6.35	6.30	500		1.94
200	5.8	6.00			

IV*b*. $y_0 = +.0325\,cm.$

Load in Grams.	Deflections.	
	Observed.	Calculated.
0	12.60	15.65
25	——	22.60
50	29.85	36.10
75	——	62.75
100	Beyond limits of balance.	130.5
200	Beyond limits of balance.	116.0
225	——	57.0
250	36.25	32.95
300	16.55	15.05
350	——	8.65
400		5.47
500		2.82

quite accurately by holding one end of the beam stationary as near as possible and taking observations with micrometer microscopes on the distortion produced in both ends and the middle of the beam while known loads are added to the free pan. A value of K' thus determined does not aid in solving for the other quantities but gives a good check on either of the above methods of solution.

The method followed was to estimate K'/K. For a uniform beam this ratio, derived from the equation of the elastic curve of a uniform beam, is $\frac{8}{3}$. The beam used was heavier and more rigid in the middle and after some study the value 4.4 was assumed. This gave for the adjusted values $y_0 = .0807$ cm., $y_0' = -.00824$, $K = .0000054$, $K' = .0000238$ cm. A later experimental determination of K', made as described above, gave $K' = .000024 \pm .7$ per cent.

The larger differences found between the experimental points and the theoretical curve IV*b* are easily accounted for by the fact that the balance was in a very sensitive condition and was somewhat uncertain. This uncertainty may have been due to some extent to the effect of the imperfect knife edges.

Theoretical curve IV*b* reaches infinity between 148.2 and 148.5 grams load.

WASHINGTON STATE COLLEGE,
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PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

THE CONDUCTIVITY OF THE AIR DUE TO THE SULPHATE OF QUININE.[1]

BY FANNY COOK GATES.

THE fact that the sulphate of quinine, when heated over 100° C. and allowed to cool, becomes phosphorescent and at the same time makes the surrounding air a conductor of electricity, has been the subject of a former investigation.[2] As a result of that study it was found that the ionization due to this cause has none of the characteristic properties of that due to the radiations from radioactive bodies. No satisfactory explanation of its cause was obtained although the following possible ones were suggested: (1) The conductivity of the air may be directly due to a chemical reaction in the quinine, possibly to simple hydration which is known to take place during the observed temperature change; (2) It may be caused by short ultra-violet light waves accompanying the phosphorescence, such as are known to produce ionization when they strike a negatively charged surface.

Hoping to find which of these theories might be correct, further tests were made with results as described below.

It was argued that the ultra-violet light theory would have to be rejected, if it were found that the conductivity of the air could be produced under conditions which give no trace of phosphorescence or if it could be proved directly that no ultra-violet light is present. Following these two possibilities in turn, tests were first made at low pressures.

The effect of reducing the pressure was found to greatly increase the ionization current so long as the quinine was heated in the open air before placing it in the testing vessel and exhausting. When heated electrically within the vessel at a low pressure, hardly any ionization current could be detected and it could always be entirely stopped by reëxhaustion. By keeping the quinine in this state for a half hour or more and

[1] Abstract of a paper presented at the meeting of the Physical Society held on October 28, 1905.

[2] PHYSICAL REVIEW, March, 1904.

then allowing fresh air to enter the chamber, both the ionization and the phosphorescence resulted as with normal cooling.

Observations of the effect of cooling in damp and in dry air at atmospheric pressure showed that neither the electrical nor the optical effect could be obtained when the quinine was heated in a vessel in which P_2O_5 had been kept for several hours. Both effects were hastened when the quinine was cooled in air saturated with water vapor.

The alkaloid of quinine was sprinkled over a piece of asbestos saturated with sulphuric acid and placed between the plates of the testing vessel, but no ionization of the air could be detected during the forming of the quinine sulphate.

These observations gave such strong evidence that hydration was the cause of the phosphorescence, if not directly of the ionization, that an attempt was made to produce them without heating the quinine. Unheated quinine was kept over night in the testing vessel containing P_2O_5. The next morning, without heating the quinine, damp air was pumped into the vessel and ionization at once began and continued as before. A similar effect was produced on the phosphorescence. Thus all attempts at producing one effect without the other were unsuccessful and lead us to conclude that either the ionization is due to ultra-violet light accompanying the phosphorescence or that each is caused by hydration, independently of the other.

Direct tests for ultra-violet light, by exposing photographic plates to the phosphorescent light after it had travelled through quartz, showed no difference in the darkening of the plates from that which occurred when the quartz was replaced by glass or by air.

Tests were made with the upper plate of various materials and surfaces. Plates of zinc, brass, iron and platinum gave equal ionization currents and the ratio of the currents obtained when the lower plate was charged positively and negatively remained constant for the various plates. A surface covered with lamp-black and again with soap-film produced no change. Therefore these direct tests gave no indication of the presence of ultra-violet light.

These experiments were made in the Cavendish laboratory and I desire to express my gratitude and appreciation to Professor J. J. Thomson for his stimulating interest and advice during their progress.

Electrolytic Mercurous Sulphate as Depolarizer for Standard Cells.[1]

By George A. Hulett.

THE problem of increasing the reproducibility of the unit of electromotive force was taken up two years ago. It had been supposed that the depolarizer was responsible for variations in the E.M.F. of standard cells and accordingly a study of mercurous sulphate, the depolarizer, was undertaken. The preliminary work showed that various samples of "chemically pure" mercurous sulphate gave variations of over a millivolt in cells in which the other materials were all the same, and it therefore seemed necessary to have a sample which would serve as a standard of reference. In order to obtain as pure a product as possible the following electrolytic method was devised.

Mercury to the depth of 2 cm. was placed in the bottom of a battery jar and over this was poured dilute sulphuric acid (1 to 6 by vol.) to a depth of 12 cm. The mercury was made the anode and a platinum wire which dipped into the acid served as cathode. As soon as the solution became saturated with mercurous sulphate, the salt began to deposit in the form of small grayish crystals. It was found necessary to provide the apparatus with a motor driven stirrer, so arranged that the L-part of the stirrer passed close to the surface of the mercury, and at a rate sufficient to prevent the solid sulphate from interfering with the anode reaction (about 150 revolutions a minute). The current density was .30 amp. per 100 cm.^{2} of mercury surface. Later results show that with lower current densities a clear white product is formed, but when this is used as depolarizer the cells have a higher and more variable E.M.F. Another important point developed by later work is that the acid used must be of greater than molecular concentration in order to avoid hydrolysis.[2]

The first mercurous sulphate used was, by chance, prepared under these essential conditions, and also precautions were taken to prevent hydrolysis by washing with a cadmium sulphate solution instead of water. This preparation was used in constructing the *D* series of four cadmium cells which were set up December 21, 1903. Materials similarly prepared were used in the *F* series of ten cells (February 15, 1904). All these cells were in perfect agreement and showed their constant value at once. On March 15, 1904, ten Clark cells were made in which the above electrolytic mercurous sulphate, washed with zinc sulphate solution, was used.

A report on these cells was made by Professor Carhart at the Wash-

[1] Abstract of a paper presented at the meeting of the Physical Society held on October 28, 1905.

[2] Hulett, Zeitsch. f. Phys. Chem., 49, 483, 1904.

ington meeting of the American Electrochemical Society,[1] and also a paper was read at the International Electrical Congress of St. Louis, September, 1904. The cells have now been under observation for nearly two years and some idea of their constancy and temperature coefficient can be given. The agreement of the *D* and *F* series has been exceptional as variations of single cells are not over 2 parts in 100,000, but the Clark cells are not so constant as they show variations of about 5 parts in 100,000, disregarding the temporary variations due to the generation of gas at the zinc amalgam. The following table gives the values at different temperatures, taken as a mean of a large series of observations :

Temperature in Degrees.	Cadmium Cells, D and F Series.		Clark Cells, H Series.	
	Observed.	Calculated.	Observed.	Calculated.
18.0	1.01921	1.01921	1.43025	1.43021
21.1	1.01908		1.42633	
25.0	1.01893	1.018925	1.42136	1.42125
29.85	1.01870	1.01869	1.41470	1.41464

The calculated values were obtained by using the accepted temperature coefficients, and starting from the observed value at 21.1°, the temperature at which the first comparisons were made. It will be seen that the calculated values for the Clark cells are in fair agreement with the observed, while in the case of the cadmium cells the agreement is excellent. The observed values were obtained by comparison with some older cadmium cells of Professor Carhart's; these cells were made in the usual way and their value at 21.1° was taken to be 1.01936 int. volts, assuming that the Clark cell at 15° has an E.M.F. of 1.434 volts, and that the ratio of the Clark at 15° to the cadmium at 20° is 1.4067.[2] Professor Carhart kindly consented to compare these cells with his and the observations at 21.1° were made in the physical laboratory. The other observations were made by myself in the laboratory of physical chemistry at the University of Michigan. It is to be noted that the cells made with electrolytic mercurous sulphate as depolarizer are lower by .00028 volt than cells made in the usual way, and it might be added that they assumed their constant value at once, while it has been necessary to allow cells made in the old way to "age," that is they have too great an E.M.F. at first and gradually settle down to a constant value.

During the summer of 1905 it was necessary to transport the cells from Ann Arbor to Princeton, and precautions were taken to prevent jarring by packing the cells in cotton and by fastening rubber stop-

[1] Trans., vol. 5, 59, 1904.

[2] Jaeger and Lindeck, Zeitsch. f. Instk., 21, 73, 1901.

pers to the bottom of the box. Comparisons made since arriving in Princeton show no effect of travelling, but there is evidence from other experiences which shows that jarring may alter the E.M.F. for a considerable time.

Dr. K. E. Guthe, of the Bureau of Standards, was redetermining the absolute value of the cadmium cell with a newly constructed electrodynamometer, and wished to compare his cells with mine. On the way to Princeton, a stop was made at Washington for this purpose, and two of the *F* series and some Clark cells were left with Dr. Guthe. By letter Dr. Guthe informs me that the value of the *F* series at 25° is 1.01836 absolute volts, and the cadmium cells made in the old way would be 1.01864, or .00025 volt higher than the value given by Jaeger and Lindeck (l. c.). Dr. Guthe will soon publish his results in full.

The Clark cells have a larger temperature coefficient and are not as reproducible as the cadmium cells, also there is a slow generation of gas at the zinc amalgam, which often forces the solid zinc sulphate away from the amalgam and changes the E.M.F. or breaks the contact. This difficulty may be corrected by warming this leg to 40° and allowing the gas to escape to the upper part of the cell. A more serious difficulty has arisen from the great tendency of the Clark cells to crack at the zinc side. Lord Rayleigh has attributed this to an alloying of the zinc with the platinum, causing it to expand and crack the glass. I have found that this difficulty may be easily avoided by allowing the platinum wire to extend well into the leg of the cell and covering it, except at its point, with a thin sheath of glass. This devise has now been tested for two years on my Clark cells and not one of them has cracked on the zinc side. In sealing in the platinum wire a small bead of "ruby" glass was first melted on the wire near the end, but without covering the end. A small hole was made in the leg of the cell and the bead adjusted to the hole; when the glass was quite soft the wire was pushed in to the desired position and the seal completed. In this way the wire inside the cell was covered, except at its point, with a thin sheath of glass, and the amalgam did not come in contact with that part of the wire which passed through the wall of the cell.

In many respects the Clark cell is inferior to the cadmium cell, but when both kinds are constructed, their ratio is easily and accurately determined, and this ratio gives a better criterion of the reliability of cells than can be obtained by making one kind alone. Jaeger and Lindeck (l. c.) have determined the ratio

$$\frac{\text{Clark } 15^\circ}{\text{Cadmium } 20^\circ} = 1.4067,$$

and the results so far obtained give the following values for this ratio at three temperatures:

$$\frac{\text{Clark } 18^\circ}{\text{Cadmium } 18^\circ} = 1.4033.$$

$$\frac{\text{Clark } 21.1^\circ}{\text{Cadmium } 21.1^\circ} = 1.3997.$$

$$\frac{\text{Clark } 25^\circ}{\text{Cadmium } 25^\circ} = 1.3949.$$

When this ratio is determined over a greater range, the equation of the change of the ratio with the temperature may be given.

An attempt was made to simplify the construction of standard cells by forming the depolarizer in the cell after it had been set up. The combination — mercury | cadmium sulphate, solution | cadmium amalgam — was constructed and a current of .005 amp. passed through the cell from the mercury to the cadmium sulphate solution. The solution soon began to deposit the depolarizer at the surface of the mercury, and after about 50 mg. had been deposited the current was broken. The observations on this cell from the time of breaking the current were:

	12 Hour.	2 Hours.	1 Day.	3 Days.	15 Days.	30 Days.
July . . .	1.0201	1.0198	1.0196	1.0194	1.0193	1.01915

This cell never showed a constant value, the salt formed was decidedly yellow and evidently not normal mercurous sulphate. An old cell was then taken and reversed with a current of .0005 amp. for several hours, but the same yellow salt appeared, the E.M.F. was high and is still .00015 volt above its mates.

In order to obtain a depolarizer which would be in equilibrium with a cadmium sulphate solution, the system — mercury, mercurous sulphate, cadmium sulphate and solution — was rotated at 25° for two weeks. The mercuous sulphate from this system was used as depolarizer in cells I_6, I_7 and I_8. The following observations were made:

		3 Days.	7 Days.	30 Days.	45 Days.	2 Months.	3 Months.	11 Months.
I_6	1.0204	1.0200	1.0198	1.0199	1.0197	1.0196	1.0195	1.0190
I_7	1.0204	1.0200	1.0199	1.0199	1.0198	1.0196	1.0195	1.0189
I_8	1.0203	1.0200	1.0199	1.0200	1.0197	1.0197	1.0195	1.0191

These results were surprising as it was expected that the above described system had had time to come to equilibrium, and that the mercurous sulphate when used as depolarizer in cells, would show a constant value from the time the cells were put together. It will be seen from the above results that this is far from the case, and it suggests that the cathode leg of the cadmium cell is not a system in final equilibrium. There may be equilibrium at the boundary between the mercury and

paste and another different equilibrium in the upper part of the paste. It is best to have the paste at least one centimeter deep in the cathode leg of the cell. Some cells have been made with a small amount of paste, 2 or 3 mm. deep, and were found to be in poor agreement and variable. This behavior is explicable on the above assumption and demands that attention be given to the depth of paste necessary to give constant results. At present the greatest difficulty is in making the mercurous sulphate and in preparing the paste. This difficulty might be entirely avoided if one could procure reliable paste ready for use, and this is possible since a large amount of electrolytic mercurous sulphate might be prepared, properly washed and made to a homogeneous paste. This stock paste could be tested and the value of cells made from it determined. About a year ago some paste was made, and the cells made from it at various times have agreed to the fifth decimal place. Experiments on the effects of slight impurities in the cadmium amalgam and cadmium sulphate have been made and show that these materials of sufficient purity may easily be prepared.

NEW BOOKS.

Mathematische Einführung in die Electronentheorie. By Dr. A. H. BUCHERER. Leipzig, B. G. Teubner, 1904.

The theory of the effects due to the motion of electrically charged bodies is so full of interest, on account of the light it throws on the nature of Cathode, Becquerel and Röntgen rays, that every serious student of physics will welcome Dr. Bucherer's attempt to furnish, in a compact and convenient form, a mathematical introduction to the theory of electrons. The subject is one of considerable difficulty and at first attracted little attention, so that, till recently, only a few problems had been solved by Oliver Heaviside, J. J. Thomson and other pioneers. Now, however, the interest in the dynamics of electrons increases with each physical discovery in this field, and many mathematicians are attacking the problems and substantial progress is being made. Much of the more recent work is of a highly analytical character and an account of it would have been out of place in a book intended to serve as an introduction to the subject. Yet the reader who makes his first acquaintance with the subject from this book will not find his task always an easy one, even though the author has wisely limited his choice to those problems which admit of *comparatively* simple solutions.

The most active expounders of the theory of electrons aspire to make it give an account of the nature of ponderable matter and so to bring the whole of physical science within its domain. This is a high aim, but a theory as fundamental as that of electrons must either aim at embracing the universe or else stand self-condemned. The author, no doubt, felt bound to give a short discussion of the connexion between electrons and ponderable matter, but I shall make only this brief reference to it, as I am not competent to make any remarks upon it.

The electrical charges, whose motions are considered in this book, are either concentrated at mathematical points or are spread over spherical or ellipsoidal surfaces. For many purposes the volume of the electron may be treated as infinitesimal, but in the calculation of the energy of a moving electron or of the energy thrown off in the form of Röntgen rays, when the electron is suddenly brought to rest, it is necessary to take an electron of finite dimensions. In these cases the author follows the usual practice and assumes the electron to be a uniformly charged sphere.

After some introductory matter, Dr. Bucherer considers the steady

rectilinear motion of a system at any speed (u) less than that of light (v), and obtains the general vector equations

$$4\pi v^2\mathbf{D} = V\mathbf{Hu} + \mathbf{F}, \qquad \mathbf{H} = 4\pi V\mathbf{uD} + \mathbf{R}. \tag{1}$$

Here **H** and **D** are the values, in electromagnetic units, of the magnetic force and the electric displacement and $V\mathbf{Hu}$ denotes a vector product, **heavy type** denoting vectors. The quantities **F** and **R** are the mechanical forces experienced by a unit charge and a unit pole respectively, when moving at speed u along with the system. They are derivable from two *independent* potentials, ψ and φ, so that

$$\mathbf{F} = -\nabla\psi, \qquad \mathbf{R} = -\nabla\varphi. \tag{2}$$

Taking the axis of x parallel to **u**, and writing $1 - u^2/v^2 = s$, the fundamental equations

$$\operatorname{div}\mathbf{D} = \rho, \qquad \operatorname{div}\mathbf{H} = 0. \tag{3}$$

lead to the equations

$$s\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} = -4\pi v^2 s\rho, \tag{4}$$

$$s\frac{d^2\varphi}{dx^2} + \frac{d^2\varphi}{dy^2} + \frac{d^2\varphi}{dz^2} = 0. \tag{5}$$

Hence, when any value of φ satisfying (5) is known, *any* arbitrary value of ψ will furnish the solution of *some* problem, for (1) and (2) will give the values of **D** and **H**, and (3) the value of ρ at every point. The value of φ is quite independent of the distribution of ρ, so that φ does not arise from the motion of any system of electrical charges, and hence can arise only from a magnetic system. Thus φ may be put equal to zero when the motion of a purely electrical system is concerned. To get rid of φ, the author assumes (p. 29) that **H** is everywhere perpendicular to **u** and deduces that

$$\operatorname{div}\mathbf{R} = \operatorname{curl}\mathbf{R} = 0. \tag{6}$$

from which it follows that **R** is constant. In the text the author excludes a finite value for **R** on the ground that this would imply an infinite amount of magnetic energy. But this case simply corresponds to the motion of a system of charges in a *uniform* magnetic field. In a short table of errata he states that (6) implies that **R** is zero, but this is clearly an oversight. Though it is not obvious at first sight that **H** is everywhere perpendicular to **u** for any general system of charges, the property becomes evident if we start with a point-charge. For the magnetic force due to a point-charge in steady motion is in circles in planes perpendicular to **u**, and hence the magnetic force due to any number of point charges is also at right angles to **u**. In fact, when, as in this case

$\mathbf{R} = 0$, the lines of magnetic force are the lines in which the surfaces of constant ψ are cut by planes perpendicular to $\mathbf{u}$.[1]

Throughout the book μ is taken to be unity and hence $\mathbf{H}$ is written for $\mathbf{B}$. This leads to unsymmetrical expressions like $V\mathbf{HD}$ (in place of $V\mathbf{BD}$) and thus to some loss of clearness. In this review I have, however, followed the author's notation.

The author then gives the solutions for a point charge and for a charged ellipsoid of revolution and calculates the energy of the system in the latter case. For a sphere of radius a with a charge of q *electromagnetic* units, the magnetic part of the energy comes to

$$T = \frac{q^2v^2}{8a}\left[\left(\frac{v}{u} + \frac{u}{v}\right)\log\frac{v+u}{v-u} - 2\right]$$

$$= \frac{q^2u^2}{3a}\left(1 + \frac{6}{3\cdot 5}\cdot\frac{u^2}{v^2} + \frac{9}{5\cdot 7}\cdot\frac{u^4}{v^4} + \cdots\right),$$

while the total energy is

$$\frac{q^2v^2}{2a} + \frac{q^2v^2}{2a}\left(\frac{v}{u}\log\frac{v+u}{v-u} - 2\right)$$

or

$$\frac{q^2v^2}{2a}\left(1 + \tfrac{2}{3}\cdot\frac{u^2}{v^2} + \tfrac{2}{5}\cdot\frac{u^4}{v^4} + \cdots\right).$$

The momentum of a moving electron and the idea of electromagnetic mass are next brought before the reader. Earlier in the book it is shown that the force experienced by any system of charges and due to electromagnetic action, together with the force

$$\frac{d}{dt}\int V\mathbf{DH}\,d\tau$$

taken throughout the volume enclosed by any surface S enclosing the system, the element of volume being $d\tau$, is equivalent to the resultant of the Maxwell stress over S. Here the differentiation with regard to the time is to be performed on the values of $\mathbf{H}$ and $\mathbf{D}$ at points *fixed in space*.

The distinction between $d\mathbf{H}/dt$ at a fixed point and $d\mathbf{H}/dt$ at a point moving with the system has been overlooked by the author in an application of this result to the case of a charged body in uniform motion when S is made to ultimately coincide with the surface of the body and when both $\mathbf{D}$ and $\mathbf{H}$ vanish at all points within the surface of the body. Since $\mathbf{D}$ and $\mathbf{H}$ vanish within the body, and since $d\mathbf{D}/dt$ and $d\mathbf{H}/dt$ also vanish *within* S, he concludes that the force on the charge carried by the

[1] Phil. Trans. Royal Society, 1896, p. 700.

body is simply that due to the Maxwell stress acting over S. But the values of $\mathbf{D}$ and $\mathbf{H}$ at a *fixed point* change suddenly as the surface passes over the point and thus $d\mathbf{D}/dt$ and $d\mathbf{H}/dt$ have infinite values though only for an infinitely short time. The part of $(d/dt)\int V\mathbf{DH}d\tau$ corresponding to each element of the surface can be found by assuming the charge to form a layer of very small thickness.[1] If $\mathbf{D}_0$ and $\mathbf{H}_0$ denote the values of $\mathbf{D}$ and $\mathbf{H}$ just outside the layer, and if the outward normal make an angle θ with $\mathbf{u}$, then the force which has been overlooked is equal to

$$u\int V\mathbf{D}_0\mathbf{H}_0\cos\theta\, dS.$$

In the case of a changed sphere in steady motion, it is easily seen, from symmetry, that the surface integral $u\int V\mathbf{D}_0\mathbf{H}_0\cos\theta dS$ vanishes, when the electric and magnetic forces are entirely due to the charge on the sphere.

The force $(d/dt)V\mathbf{DH}$ per unit volume is perhaps most easily understood if we follow Heaviside and regard it as the sum of the two forces, $Vd\mathbf{D}/dt\cdot\mathbf{H}$ and $V\mathbf{D}\cdot d\mathbf{H}/dt$, the former arising from the action of the magnetic field on the electric current $d\mathbf{D}/dt$, and the latter from the action of the electric field upon the "magnetic current" $d\mathbf{H}/dt$. [Author's units.]

The author next supposes that the surface enclosing the system of moving charges is everywhere at an infinite distance from the system, and states that the resultant of the Maxwell stress over this surface vanishes. The resultant certainly vanishes when the motion is *steady* and the velocity is less than that of light, because E and H are then of the order r^{-2} and thus the force per unit area is of the order r^{-4}. But when the electron has acceleration, waves travel out from it at the speed of light and in these waves both E and H vary as r^{-1}, when r is very great. Thus, without special examination the resultant of the Maxwell stress over the surface cannot be equated to zero even though the surface be at an infinite distance. Two examples will perhaps make the point clearer.

When a charged sphere of radius a is brought suddenly to rest, a spherical pulse of thickness $2a$ travels outwards with the velocity of light. The electric and magnetic forces in the pulse are given by

$$E = \frac{quv\sin\theta.}{2ra\left(1-\frac{u}{v}\cos\theta\right)}, \qquad H = \frac{E}{v},$$

where q is the charge on the sphere in e'ectromagnetic measure, u the velocity of the sphere before it was stopped, and θ the angle between the

[1] Compare Phil. Trans. Royal Society, 1896, p. 704.

outwa d drawn radius and the direction of u. Both **E** and **H** are perpendicular to **r** and to each other, **H** being along lines of latitude and **E** along lines of long tude. On account of the relation $E = vH$ and because **E**, **H** and **r** are mutually at right angles, the Maxwell stress is normal to the sphere and is equal to $H^2/4\pi$ per unit area. The vector $V\mathbf{DH}$ is also normal to the surface and its magnitude is $H^2/4\pi v$. If the resultant of the Maxwell stress, for any concent ic sphere lying between the two boundaries of the pulse, be F, it is found, on integration, that when it is measured in the direction of u,

$$F = -\frac{v}{au}(U - U_0),$$

where U and U_0 are the electric energies of the sphere in steady motion and at rest. It also appears that the value of $\int V\mathbf{DH}d\tau$ for the volume contained by a sphere of radius r diminishes by the amount $2(U-U_0)/u$, during the passage of the pulse over the sphere, when measured in the direction of u, a result due to Oliver Heaviside. Since the time of passage is $2a/v$, it follows that during this time

$$\frac{d}{dt}\int V\mathbf{DH}d\tau = -\frac{v}{au^2}(U - U_0)\mathbf{u}.$$

As the sudden stopping of a charged sphere is an extreme case, it may be useful to give the value of F, the resultant of the Maxwell stress, for an electron which at the time t has a finite acceleration in the direction of u. Measuring F in the same direction as u, its value for a sphere of large radius R at the time $t + R/v$ is, in the author's units,

$$F = -\frac{1}{4\pi}\int H^2 \cos\theta dS,$$

since **H** and **E** are tangential to the sphere when R is very great.

But by Heaviside's formula,[1] in Dr. Bucherer's units,

$$H = \frac{qf\sin\theta}{vr\left(1 - \frac{u}{v}\cos\theta\right)^3}.$$

By integration the force is found to be

$$F = -q^2v^3 \cdot \frac{4f^2}{v^4} \cdot \frac{u}{5v^5} = -Q^2 \cdot \frac{4f^2}{v^4} \cdot \frac{u}{5v^5},$$

where Q is the charge in *electrostatic* units, and $S = 1 - u^2/v^2$. A physical conception of this result is easily obtained. For if a point, start-

[1] Nature, Nov. 6, 1902, equations (12) and (14). See Nature, Nov. 13, 1902, for corrections.

ing from rest and moving with acceleration f acquire a velocity v while it passes over a distance l, then $v^2 = 2fl$ and thus

$$F = -\frac{Q^2}{l^2} \cdot \frac{u}{5vs^4}.$$

Hence F is $u/5vs^4$ times the force between two charges each of Q electrostatic units placed at a distance l apart.

When f is infinitesimal, F is of the second order of small quantities and may be neglected. The system is then said to be in a quasi-stationary state. It will be observed that a quasi-stationary state only exists when the acceleration of the electron has *never* reached a finite value within any finite time.

When the quasi-stationary condition prevails, the force due to electromagnetic action, experienced by the charged system is $(d/dt)\int V\mathbf{H}\mathbf{D}d\tau$. The force which must be applied to the system by non-electromagnetic means is thus $-(d/dt)\int V\mathbf{H}\mathbf{D}d\tau$ or $(d/dt)\int V\mathbf{D}\mathbf{H}d\tau$ taken through all space, in addition to any force required to increase the momentum of ponderable matter. Equating this force to $d\mathbf{M}/dt$, we may call $\mathbf{M}$ the electromagnetic momentum and thus

$$\mathbf{M} = \int V\mathbf{D}\mathbf{H}d\tau.$$

The author then shows that for a charged sphere in steady motion $M = 2T/u$. In the quasi-stationary condition, the force necessary to give the sphere the acceleration du/dt is $d\mathbf{M}/dt$. Equating this quantity to $m_t du/dt$, we have

$$m_t = \frac{dM}{du} = 2\frac{d}{du}\left(\frac{T}{u}\right),$$

and so obtain for the "longitudinal mass"

$$m_t = \frac{2q^2}{3a}\left(1 + \tfrac{6}{5}\cdot\frac{u^2}{v^2} + \tfrac{9}{7}\cdot\frac{u^4}{v^4} + \cdots\right).$$

When the sphere moves with uniform speed in a circular orbit there is acceleration at right angles to the path. When this acceleration is infinitesimal, the momentum of the system will at any instant have the component M_1 parallel to the tangent and an infinitesimal component M_2 parallel to the outward normal at each instant. If r be the radius of the path, the normal force required to change the direction of M_1 is M_1u/r or $(M_1/u)u^2/r$. Since u^2/r is the acceleration of the sphere we may write

$$m_t = \frac{M_1}{u}.$$

In the limit M_1 becomes equal to M for the rectilinear motion and thus we have for the "transverse mass"

$$m_t = \frac{M}{u} = \frac{2T}{u^2} = \frac{2q^2}{3a}\left(1 + \tfrac{6}{15}\frac{u^2}{v^2} + \tfrac{9}{35}\cdot\frac{u^4}{v^4} + \cdots\right).$$

It may be added that the value of the infinitesimal M_2 is easily found. For if P be the tangential force required to maintain the sphere in steady motion, P changes the direction of M_2 and thus $P = M_2 u/r$. But Pu, the activity of P, must be equal to $2q^2f^2/3vs^2$, the rate of loss of energy by radiation,[1] where f is the acceleration and $s = 1 - u^2/v^2$. Since $f = u^2/r$, we find

$$M_2 = \frac{2q^2u^2}{3rvs^2}.$$

When u is small, $M_1 = 2q^2u/3a$ and hence the resultant momentum is inclined to the direction of u at the very small angle au/rv.

When the normal acceleration in the circular orbit is finite we must take account not only of the radiated energy but also of the radiated momentum.

According to Mr. Heaviside,[2] if $\mathbf{N}$ be the momentum and W be the energy, which has been lost by radiation at any time, $v^2 \cdot d\mathbf{N}/dt = \mathbf{u} \cdot dW/dt$. Thus $d\mathbf{N}/dt$ is parallel to $\mathbf{u}$ whatever the direction of the acceleration. The equations now become

$$P = \frac{dN}{dt} + \frac{M_2 u}{r} = \frac{u}{v^2}\cdot\frac{dW}{dt} + \frac{M_2 u}{r},$$

$$Pu = \frac{dW}{dt}.$$

But $dW/dt = 2q^2f^2/3vs^2 = 2q^2u^4/3vr^2s^2$, and thus

$$M_2 = \frac{rs}{u^2}\cdot\frac{dW}{dt} = \frac{2q^2u^2}{3rvs},$$

$$P = \frac{2q^2u^3}{3vr^2s^2}.$$

The exact expression for M_2 thus differs from the approximate one by having s in the denominator instead of s^2.

The author gives the transformations by which the general equations of the field are made available for investigating the effects arising from any given motion of an electron. The electric and magnetic forces are expressed in terms of two functions $\mathbf{A}$ and φ by the equations

$$\mathbf{E} = -\frac{d\mathbf{A}}{dt} - \nabla\varphi, \qquad \mathbf{H} = \text{curl } \mathbf{A}.$$

[1] O. Heaviside, Nature, Nov. 6, 1902, equation 10.
[2] Nature, August 31, 1905.

By means of a theorem of Beltrami the values of **A** and φ at any point P at a time t are expressed as volume integrals taken through all space. Thus

$$\mathbf{A} = \int \frac{\rho' \mathbf{u}'}{r} d\tau, \qquad \varphi = v^2 \int \frac{\rho'}{r} d\tau,$$

where r is the distance from P of the element of volume $d\tau$, ρ' is the volume density and $\mathbf{u}'$ the velocity of the electrification at $d\tau$ at the time $t - r/v$. When these formulæ for the "retarded potentials" are applied to a spherical electron with a surface charge

$$\mathbf{A} = \frac{q\mathbf{u}}{r\left(1 - \frac{u}{v}\cos\theta\right)}, \qquad \varphi = \frac{qv^2}{r\left(1 - \frac{u}{v}\cos\theta\right)},$$

where r is now the great distance of P from the center of the electron and θ is the angle between $\mathbf{u}$ and the normal drawn outwards from the sphere of radius r about the electron as center.

These formulæ are then applied to find the electric and magnetic forces at a great distance from an electron moving in any way and to calculate the energy radiated from it. This part of the book will require the reader's closest attention for the inherent difficulties are very considerable. The author would have done well if he had given a fuller discussion of the processes leading up to the values of **A** and φ. In this book and in many other books and papers on the theory of electrons, Beltrami's theorem is quoted without demonstration to the discomfort of the serious student.[1]

It is to be regretted that the author has expressed many of the most important results only in complicated vector formulæ, for very considerable skill in vector analysis is required to deduce the values of the components of **E** and **H** in ordinary coördinates from these formulæ. Vector analysis is a most valuable help in these investigations, but like many another good thing, it becomes deleterious when carried to excess.

A discussion of the Zeeman effect is given and also an account of the pulse thrown off when an electron is suddenly stopped, as in the production of Röntgen rays. By Heaviside's elegant investigation,[2] that part of the energy of a sphere which is due to its motion is deduced from the energy radiated away in the pulse. The remainder of the book is devoted to discussions on the effect of motion upon optical phenom-

[1] Sommerfeld has recently given a new and brilliant proof of the formulæ for the "retarded potential" in his paper "Simplified deduction of the field and the forces of an electron moving in any given way." Proceedings of the Koninklijke Academie van Wetenschappen te Amsterdam, Nov. 26, 1904.

[2] The Electrician, Nov. 29, 1901.

ena, the connexion between ponderable matter and electrons and on the theory of optical dispersion.

The book thus covers a wide range of most interesting work and the author may be warmly congratulated upon having made an excellent selection of subjects.

In the second edition, which will probably be demanded, the author would have the opportunity of adding further explanations where they are needed and of correcting several misprints and small errors. He does not appear to have had any assistance in correcting for the press, and it is hardly ever wise for an author to trust entirely to his own reading of the proofs.

In its present form the book is useful and, taken as a whole, is reliable. In a revised form it might be made a most valuable text book, not too difficult for students of moderate mathematical skill, and it would then satisfy a real want.

The book is the work of one of my intimate friends. For this, as well as for other reasons, I wish it much success.

G. F. C. SEARLE.

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Lehrbuch der Physik. Von O. D. CHWOLSON, Band III. Braunschweig, Vieweg, 1905. Pp. xii + 988.

The first two volumes of Professor Chwolson's treatise were translated into German by Dr. Pflaum of Riga. The translation of Volume III., which deals with the subject of heat has been admirably done by Dr. Berg of the Central Observatory in St. Petersburg.

In the introduction to chapter I., heat is described as a type of kinetic energy due to an irregular unsystematic motion of the separate particles of a body as distinguished from the motions which these particles undergo when the body moves as a whole and from regular or systematized motions such as the vibratory motions which give rise to sound waves, etc. All motions of matter which are not heat motions tend to go over into heat motion and all other forms of energy due to the motion of matter tend to transformation into heat energy. This preliminary definition of heat is followed by the consideration of temperature and the means of measuring temperature including electrical and optical pyrometry.

Chapter III. deals with the study of the expansion of solids, liquids and gases and chapter IV. with thermal capacities and specific heats.

At this point in his treatise the author introduces a variation in the traditional development of the subject in the form of a brief chapter on the transformation of various forms of energy into heat energy. The conversion of kinetic energy, due to motions of translation and rotation, of radiant energy and of the energy of the electric current and electric

discharge are briefly outlined and the remainder of the chapter is given up to thermochemistry. Chapter VI. treats of the laws of cooling of bodies and chapter VII. to thermal conductivity.

The remainder of the volume, comprising about 500 pages, deals with hermodynamics and its applications including much new material, not found in previous general treatises on physics, concerning the liquefaction of gases and the properties of liquids and vapors at the critical point.

The volume closes with a very full and satisfactory discussion of the equilibrium of substances in contact, the phase rule and the phenomena and theory of solutions. E. L. N.

The Study of Chemical Composition. By IDA FREUND. Pp. xvi + 650. Cambridge Physical Series. The University Press, Cambridge.

This book presents in a clear and orderly manner the historical development of the theories of the constitution of matter. The attitude of the writer is that of the philosopher rather than that of the physicist or the chemist. Thus the growth of the thoughts and ideas is given the prominent place, a fact which should make the book of considerable interest to physicists and chemists.

The work begins with a chapter on the methods of modern science and the relations of theory and hypothesis. The early theories of combustion are then taken up. The phlogistic hypothesis is treated in a manner to allow of a keen appreciation of the point of view of the early workers. Lavoisier, Berthollet, Richter, Dalton, Proust, Stas and others are quoted as the author shows the development of the idea of equivalent and combining weights. Chapter VIII., with which this part of the book is concluded, deals with combining weights in a way that will be of interest to chemists.

Chapters IX. to XIX. include the development of the conceptions of the ultimate constitution of matter and the theories which in one way or another have tended to throw light upon that idea. The views of the very earliest thinkers are taken up first. Then the atomic hypothesis of Dalton, the hypotheses of Gay Lussac and Avogadro, the law of Dulong and Petit, Mitscherlich's views of the connection between crystal form and chemical composition, the periodic law, the doctrine of valency, isomerism, etc., are clearly discussed. The last chapter gives a well balanced exposition of the hypothesis of the genesis of the elements according to contemporaneous writings. Radioactivity and the modern conceptions of the complex atom are discussed quite at length.

The work is unique, in that it contains numerous and full quotations and a great deal of data taken from the original literature.

The work will commend itself to scientists interested in the problems which are related to chemical composition and to the constitution of matter. W. C. GEER.

Atlas of Emission Spectra. HAGENBACH and KONEN. Authorized English edition by ARTHUR S. KING. London, Wm. Wesley & Son, 1905. Pp. vii + 70.

The twenty-eight photographic plates which make up this atlas afford admirably executed illustrations of the arc and spark spectra of nearly all the known chemical elements. The completeness of the collection is indeed one of its admirable features. The only elements not represented by photographs are fluorin, gallium, germanium, krypton, neon, radium, scandium, tantalum, thulium and xenon. Two plates are as a rule devoted to each spectrum, one extending through the ultra-violet and violet, the other through the blue, green, yellow and orange. The 70 pages of text accompanying the charts themselves are given up to a description of the way in which the photographs were prepared and arranged; with directions for using the various charts. There is an alphabetical list of the elements represented, an index showing the spectra given on each plate and a brief descriptive table in which the charts are taken up in order and their characteristic features are indicated.

E. L. N.

Experimentelle Untersuchung von Gases. MORRIS W. TRAVERS. Braunschweig, Vieweg & Son, 1905. Pages xii + 372.

This German translation by Dr. Estreicher of Travers' well-known volume on the study of Gases is a tribute on the part of continental physicists to an author the good qualities of whose work were immediately recognized by every English speaking physicist. The German edition has been carefully brought up to date. Dr. Estreicher has added a new chapter on the heat of vaporization of liquefied gases, in which the methods of Shearer and of Fischer and Alt are described and a comparison made with the results obtained by himself. E. L. N.

Differential Equations — a short course for engineering students. By JAMES E. BOYD. Published by the author, Ohio State University, Columbus, Ohio, 1905. Pp. vi + 54.

The range of this book is indicated by the titles of its four chapters. These are: *differential equations of the first order and degree, equations of the first order and higher degrees, differential equations of order higher than the first, linear differential equations of higher order with constant coefficients.* But little attention is given to theoretical considerations. The merit of the book consists in the large number of mechanical and

electrical problems that are given. These ought to do much to stimulate the interest of the students for whom the author writes.

There is one serious defect that ought to be mentioned. On page 8 the author starts out to prove that an equation of the form

$$Mdx + Ndy = 0$$

is exact if

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x};$$

but, as a matter of fact, he proves the converse of this.

WILLIAM BENJAMIN FITE.

Die Elektrischen Bogenlampen. VON J. ZEIDLER. Braunschweig, Vieweg & Son. Pp. x + 143.

This little volume, which forms the sixth number of Dr. Benischke's series of handbooks of electrotechnics, treats in brief form of the arc lamp. The work is divided into four parts, the first and shortest of which contains a discussion of the electrical principles of arc lamps and arc lamp circuits. Part two, which deals with construction, is divided into three sections devoted respectively to open arcs, flame arcs, and enclosed arcs. This portion of the book is of a practical and descriptive nature and is representative essentially of arc lamp construction as it is known in the present day in Germany. The third part of the volume has to do with photometry and the application of arc lights in illumination. It is, in some respects, the most useful of all in that it deals in a practical and reasonably thorough manner with a problem which has hitherto been greatly slighted by writers on these subjects. The fourth and concluding part of Dr. Benischke's handbook deals with the installation of electric arc lamps. E. L. N.

Wireless Telegraphy, its History, Theory and Practice. By A. FREDERICK COLLINS. 8vo, pp. xi + 299. New York, McGraw Publishing Co. 1905.

In the opinion of the reviewer, the illustrations, over three hundred in number, constitute the most useful part of this book. The author has evidently devoted much time to this feature, and among the numerous diagrams and reproductions of photographs are many that could not readily be found elsewhere. Unfortunately the reproductions are often not well printed. Possibly the paper is to blame for this. Many of the photographs also, although of a kind that is not unusual in the technical press, can scarcely be looked upon as adding to the value of the book from either a scientific or technical point of view. Fig. 164, entitled

"The Marconi System," is a good example of this class of illustrations. The half-tone represents Mr. Marconi seated at a table and thoughtfully nspecting the tape from a Morse recorder, while grouped about him are various pieces of electrical apparatus, whose nature and purpose are left to the reader's imagination. The "Fessenden System" (Fig. 205), the "Guarini Transmitter" (Fig. 172), and the "Collins Wireless Telephone" (Fig. 332), are illustrated in an equally lucid manner.

For one not already possessing some familiarity with the subject of electrical waves the book would prove entirely useless. The lack of any logical sequence in the discussion is in itself sufficiently confusing. But far more serious is the lack of clearness in the explanation of difficult points, a fault which is accentuated by carelessness in style. The book gives the impression of having been written in a hurry, after an extended but superficial examination of the literature of the subject. A few illustrations of statements follow, which are, to say the least, confusing: "Fitzgerald employed a sensitive galvanometer as a detector, the field of force created by the oscillations exerted a final influence through the galvanometer system."[1] "The monochromatic oscillator may therefore be compared to an octave of musical notes, each producing a distinct wave-length" (p. 59). "All the oscillator systems described above are known as *open circuit oscillator systems*, that is to say, they have a free period of oscillation, and therefore radiate waves with great energy, though the oscillations are quickly damped out. There is another class of oscillators termed "*closed circuit oscillator systems*, in which the period of oscillation is limited to the size of the circuit. If this has a natural period equal to that of the impressed oscillations these will be prolonged for a considerable length of time before the energy is dissipated; closed-circuit oscillators are, therefore, very feeble emitters of electric waves" (p. 61). Statements of an equally confusing character are to be found on almost every page. In reading such statements the reviewer is reminded of the quotation from Faust with which Boltzmann begins the preface to his "Vorlesungen über Maxwell's Theorie der Elektricität und des Lichtes," a quotation which would seem particularly appropriate in the case of the book now under consideration.

In the hands of one whose familiarity with the subject enables him to interpret the many obscure passages and to distinguish the inaccurate statements from those that are correct, Mr. Collins's book may in some cases be found useful. But in my opinion the field of its usefulness is very limited.

ERNEST MERRITT.

[1] This remarkable sentence (p. 148) contains all that is said regarding Fitzgerald's detector.